TECHNICAL METHODS

OF

CHEMICAL ANALYSIS

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ENGLISH TRANSLATION

FROM THE LATEST GERMAN EDITION, ADAPTED TO ENGLISH
CONDITIONS OF MANUFACTURE

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VOLUME III.—PART I.

GURNEY AND JACKSON

PREFACE

THE sections comprised in this third and concluding volume of the English edition are included in the third and fourth volumes of the last German edition, published in 1910-11.

The sections on "Brewing Materials and Beer" and on "Vinegar" have been entirely re-written for the English edition, as the processes of manufacture and associated methods of analysis that obtain in this country are so entirely different from those of Germany; and the sections on "Spirits" and on "Brandy and Liqueurs" of the German edition have been combined into one section under the title of "Alcohol, Potable Spirits, and Liqueurs," and have been fully revised, so as to provide a connected account of the analytical methods required by the English conditions of manufacture and of legislative control.

All the remaining sections have been submitted to English experts for revision. The contents of the volume have thus been brought thoroughly up to date by the addition of all relevant matter of importance since the issue of the last German edition.

Also, the order of the sections in the German edition has been altered, with the object of securing a somewhat better sequence of the subject matter.

With the exception of those cases in which empirical factors are employed in technical work, all the numerical data are calculated from the table of atomic weights for 1914, issued by the International Committee, with $O = 16$ as the basis. As in Volumes I. and II., the numerical data for gases, and for the weights of substances to be taken for analysis so as to correspond to definite volumes of gases,

are calculated from the *real* litre weights according to the most reliable determinations, not from the calculated values. Also, all temperatures are given in Centigrade degrees, except where otherwise stated.

The Editor desires to record his thanks to Mr J. S. S. Brame, Lecturer on Fuel, The Sir John Cass Technical Institute, for very kindly reading the proofs of the sections on "Mineral Oils" and "Lubricating Oils," the MSS. of which had been revised by the late Dr Lewkowitsch; to the Director of Navy Contracts, for a copy of the Admiralty specification governing the supplies of manufactured rubber; and to Mr L. Archbutt, for permission to reproduce the illustration of his vaporimeter. Also to Messrs Baird & Tatlock, Messrs A. D. Cillard (Paris), Messrs Constable & Co., and Messrs C. Griffin & Co., for the loan of and permission to reproduce blocks; and to Messrs Macmillan & Co., for permission to reproduce a block from their publication, *India-rubber Laboratory Practice*, by W. A. Caspari.

<div style="text-align:right">CHARLES A. KEANE.</div>

'LIST. OF CONTRIBUTORS TO THE GERMAN EDITION, AND OF REVISERS AND AUTHORS OF THE ENGLISH TRANS-LATION IN VOL. III.

Mineral Oils.
By Prof. D. HOLDE, Lichterfelde.
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Lubricants.
By Prof. D. HOLDE, Lichterfelde.
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Oils, Fats, and Waxes.
By the late J. LEWKOWITSCH, Ph.D., M.A.
Revised by The Author.

Special Methods of Analysis Employed in the Oil and Fat Industries.
By the late J. LEWKOWITSCH, Ph.D., M.A.
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Resins, Balsams, and Gum-Resins.
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Inorganic Colours.

By Prof. A. EIBNER, Munich.
Revised by H. J. L. RAWLINS and A. RULE, D.Sc., Ph.D.

LIST OF ABBREVIATED TITLES OF JOURNALS

JOURNALS.	ABBREVIATIONS.
Acetylene	Acetylene
American Chemical Journal	Amer. Chem. J.
American Journal of Science	Amer. J. Sci.
Analyst	Analyst
Annalen der Chemie	Annalen
Annalen der Physik	Ann. Physik
Annales de Chimie analytique appliquée à l'Industrie, à l'Agriculture, à la Pharmacie et à la Biologie . .	Ann. Chim. anal.
Annales de Chimie et de Physik	Ann. Chim. Phys.
Annales des Falsifications	Ann. Falsific.
Archiv der Pharmacie	Arch. Pharm.
Atti della Reale Accademia dei Lincei	Atti R. Accad. Lincei
Berg und Hüttenmännische Zeitung	Berg u. Hütten. Zeit.
Berichte der deutschen chemischen Gesellschaft . .	Ber.
Biedermann's Zentralblatt für Agricultur Chemie . .	Biedermann's Zentr.
Bollettino chimico farmaceutico	Boll. chim. farm.
Brewer's Journal	Brewer's J.
British and Colonial Druggist	Brit. and Col. Drug.
Bulletin de l'Association Belgique des Chimistes . .	Bull. Assoc. Belg. des Chim.
Bulletin de l'Association chimique de Sucre et de Distillerie	Bull. Assoc. Chim. Sucr.
Bulletin de la Société chimique de Belgique . . .	Bull. Soc. Chim. Belg.
Bulletin de la Société chimique de Paris . . .	Bull. Soc. Chim.
Bulletin de la Société Industrielle du Nord de la France .	Bull. Soc. Ind. Nord
Bulletin de la Société Industrielle de Mulhouse . .	Bull. Soc. Ind. Mulhouse
Chemical News	Chem. News
Chemical Trade Journal	Chem. Trade J.
Chemiker Zeitung	Chem. Zeit.
Chemiker Zeitung Repertorium	Chem. Zeit. Rep.
Chemische Industrie	Chem. Ind.
Chemische Revue über die Fett- und Harz-Industrie .	Chem. Rev. Fett-Ind.
Chemisches Zentralblatt	Chem. Zentr.
Chemist and Druggist	Chem. and Drug.
Comptes rendus hebdomadaires des séances de l'Académie des sciences	Comptes rend.
Der Gerber	Gerber
Deutsche Gerber Zeitung	Gerber Zeit.
Die landwirthschaftlichen Versuchs-Stationen . . .	Landw. Versuchs-Stat.
Dingler's polytechnisches Journal	Dingl. polyt. J.
Electrician	Electrician
Electrochemical and Metallurgical Industry . . .	Electrochem. Ind.
Electrotechnische Zeitschrift	Electrotech. Zeitsch.
Engineer	Engineer

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Journals.	Abbreviations.
Engineering	Engineering
Engineering and Mining Journal	Eng. and Min. J.
Farben-Zeitung	Farben-Zeit.
Färber-Zeitung	Färber-Zeit.
Fischer's Jahresbericht	Fischer's Jahresber.
Gazzetta Chimica Italiana	Gazz. Chim. Ital.
Gummi-Zeitung	Gummi-Zeit.
India-rubber Journal	India-rubber J.
Industrie Blatt	Ind. Bl.
International Sugar Journal	Int. Sugar J.
Jahresbericht der chemischen Technologie	Jahresber. d. chem. Techn.
Jahresbericht der Pharmazie	Jahresber. d. Pharm.
Jahresbericht für Chemie	Jahresber. f. Chem.
Journal of Analytical and Applied Chemistry	J. Anal. and Applied Chem.
Journal de Pharmacie et de Chimie	J. Pharm. Chim.
Journal für Gasbeleuchtung und Wasserversorgung	J. Gasbeleucht.
Journal fur praktische Chemie	J. prakt. Chem.
Journal of Agricultural Science	J. Agric. Sci.
Journal of Gas Lighting	J. Gas Lighting
Journal of Industrial and Engineering Chemistry	J. Ind Eng. Chem.
Journal of Physical Chemistry	J. Phys. Chem.
Journal of the American Chemical Society	J. Amer. Chem. Soc.
Journal of the Chemical Society	J. Chem. Soc.
Journal of the Chemical Society, Abstracts	J. Chem. Soc. Abstr.
Journal of the Chemical, Metallurgical, and Mining Society of South Africa	J. Chem. Met. Soc., S. Africa
Journal of the Franklin Institute	J. Franklin Inst.
Journal of the Institute of Brewing	J. Inst. Brewing
Journal of the Institution of Mechanical Engineers	J. Inst. Mech. Eng.
Journal of the Institute of Metals	J. Inst. Metals
Journal of the Iron and Steel Institute	J. Iron and Steel Inst.
Journal of the Physical and Chemical Society of Russia	J. Russ. Phys. Chem. Soc.
Journal of the Royal Society of Arts	J. Soc. Arts
Journal of the Society of Chemical Industry	J. Soc. Chem. Ind.
Journal of the Society of Dyers and Colourists	J. Soc. Dyers and Col.
Koninklijke Akademie van Wetenschappen te Amsterdam. Proceedings (English Edition)	Proc. K. Akad. Wetensch. Amsterdam
Leather Trades Review	Leather Tr. Rev.
Le Stazioni sperimentali agrarie Italiane	Staz. speriment. agr. Ital.
Mittheilungen aus dem königlichen Materialprüfungsamt zu Gross-Lichterfelde West	Mitt. k. Materialprüf.
Mittheilungen aus der Zentralstelle für wissenschaftlich-technische Untersuchungen	Mitt. Zentralst. Wiss.-tech. Unters.
Mittheilungen des technischen Gewerbemuseums in Wien	Mitt. techn. Gew. Museums
Monatshefte für Chemie der kaiserlichen Akademie der Wissenschaften, Wien	Monatsh.
Monatsschrift für Textil-Industrie	Monatsschrift f. Text.-Ind.
Moniteur Scientifique	Monit. Scient.
Oesterreichische Chemiker Zeitung	Oesterr. Chem. Zeit.
Oesterreichisch-Ungar Zeitschrift für Zuckerindustrie und Landwirthschaft	Oesterr.-Ungar Zeitschr.
Paper and Pulp	Paper and Pulp
Papier-Zeitung	Papier-Zeit.
Petroleum Review	Petrol. Rev.

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PART I

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PART II

MINERAL OILS

By Prof. D. HOLDE, Ph.D., Divisional Director of the Royal Testing Laboratory, Gross-Lichterfelde, Berlin. English translation revised by the late J. LEWKO-WITSCH, M.A., Ph.D.[1]

CRUDE PETROLEUM, NAPHTHA, BURNING OILS, PARAFFIN WAX, ASPHALT, SHALE OIL, AND LIGNITE TAR.

A.—CRUDE PETROLEUM.

CRUDE Petroleum is usually dark brown or black in colour, but occasionally lighter-coloured varieties (pale yellow to reddish-brown) are met with. According to the filtration hypothesis of D. Day, the lighter colour of certain crude oils is to be attributed to the percolation of the oil through subterranean layers of argillaceous shale, which absorb the colouring matter. If the crude oil is allowed to percolate upwards through a column of fuller's earth in a tube, fractionation takes place to a certain extent, paraffin hydrocarbons accumulating in the lighter fraction at the upper end, and heavy, unsaturated hydrocarbons at the lower end of the tube. According to Hófer's view, however, the filtration hypothesis is not substantiated by geological observations.

Two chief types of crude oil must be differentiated :—(1) Crude oils rich in naphthenes, with a paraffin-wax content of less than 1 per cent., containing, as a rule, very small quantities of low-boiling fractions (benzine and burning oils), and rich in high-boiling lubricating oils which do not solidify readily; (2) crude oils containing less naphthenes, with a paraffin-wax content of 3-8 per cent., and yielding considerable quantities of benzine, burning oil, and light, mobile lubricating oils. Bustenari oil, however, notwithstanding its very low paraffin-wax content, yields considerable quantities (25 per cent.) of benzine.

[1] The Editor is indebted to Mr J. S. S. Brame, Lecturer on Fuel, The Sir John Cass Technical Institute, for very kindly reading the proofs of this section, the MSS. of which had been revised by the late Dr Lewkowitsch.—C. A. K.

American, Galician (Boryslaw and Tustanowice), and Roumanian crude oil (from Campina) form the chief source of good paraffin wax (for candles), burning oil, and petroleum benzine. ·

Most of the lubricating oils prepared from American, Galician, and Roumanian crude oils have a higher solidifying point (about 0°) than Russian oils. A few Galician oils, e.g. that of Grosno, and a large proportion of the Roumanian oils, namely, the oils of Bustenati, Moreni, and Tintea, making up 70 per cent. of the Roumanian production, also yield lubricating oils useful for lubricating engines, railway carriages, etc., on account of their low solidifying point, suitable viscosity, and high flashing point. For cylinder oils the highly viscous, salve-like American products have proved the most suitable. The crude petroleums from Java, Borneo, and Sumatra are noted for the considerable amounts of low-boiling hydrocarbons useful as motor oil. The crude German oils are mostly deep brown or black and somewhat viscous; those occurring in Alsatia are suitable for the preparation of benzine, burning oil, easily solidifying lubricating oils, "cleaning oils," gas oils, and asphalt; recently, also, paraffin wax has been extracted from them. The Hanoverian oils, especially the heavy oils from Wietze, yield lubricating oils, but no paraffin wax, and but very little benzine; they contain, however, notable amounts of asphaltic substances. In addition to the products enumerated above there are obtained, from crude petroleums, transformer oils, and the still residues sold as Fuel oil (Masut), Goudron, Asphalt, coke for electrodes, etc.

The world's production of crude petroleum in 1912 was 46 million tons, as compared with a production of 1050 million tons of coal. It is, however, to be remembered that the calorific value of crude petroleum is 11,000-11,100 Cal. per kilogram as against 7000-7500 Cal. for coal, and only 4500-5000 Cal. for air-dried lignite. The distribution of the world's production in 1912, expressed as a percentage of the total, was as follows:—United States 63·25, Russia 19·37, Mexico 4·71, Galicia 2·43, Roumania 3·70, East Indies 3·09, India 2·03, Germany 0·28.

I. CHEMICAL COMPOSITION.

Crude petroleum consists chiefly of hydrocarbons of various boiling points, which do not belong to the lower boiling aromatic series (difference from coal-tar hydrocarbons). The oils are not dissolved by sulphuric acid, whereas the heavier oils are partially converted into soluble sulphonic acids. Aromatic hydrocarbons (benzene and the higher homologues) occur in small quantities in certain petroleums. The chemical nature of the viscous lubricating oils of petroleum is still unknown. Benzine, burning oil, gas oil, and paraffin wax consist, in the case of Pennsylvanian petroleum, mainly of hydrocarbons of the

methane series, C_nH_{2n+2}. In the case of Russian petroleum 80 per cent. consists of naphthenes, *i.e.* alicyclic polymethylenes, such as :—

pentamethylene, $CH_2 . CH_2 . CH_2 . CH_2 . CH_2$;

hexamethylene, $CH_2 . CH_2 . CH_2 \quad CH_2 . CH_2 . CH_2$;
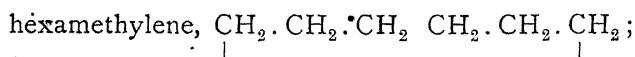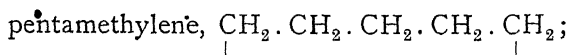
methyl hexamethylene; etc. The high-boiling fractions of the Russian oils consist essentially of polynaphthenes (perhaps hydrodiphenyls). The naphthenes resemble the paraffin rather than the benzene hydrocarbons in their chemical behaviour; they are not acted upon by permanganate, or by concentrated sulphuric acid, but yield substitution products on treatment with chlorine and bromine, and even, though with greater difficulty, with dilute nitric acid; concentrated nitric acid converts hexanaphthene into adipic acid, pentamethylene into glutaric acid. Zelinsky has succeeded in preparing synthetically high-boiling naphthenes—viz., cycloeikosan, $C_{20}H_{40}$, and cyclotessaracontane, $C_{40}H_{80}$ (melting point 118°), starting from the methyl ester of sebacic acid. As these experiments demonstrate the great tendency of the naphthenes to polymerise, Charitschkoff doubts whether the high-boiling viscous fractions of Russian petroleum consist of naphthenes, as is generally assumed. In the German, Galician, and Roumanian petroleums, the relative proportions of methane hydrocarbons and naphthenes vary according to the special localities in which the oils are found. In Galician and Roumanian oils notable quantities of unsaturated hydrocarbons occur, and in the latter aromatic hydrocarbons also. In some crude oils (especially those from Texas) secondary products occur in small quantities, such as pyridine bases, probably resulting from the decomposition of marine animals, according to the Höfer-Engler theory of the origin of petroleum, sulphur compounds such as mercaptans and organic sulphides (especially in Ohio oils), and oxygenated and sulphurised asphalt. The hydrocarbons of Texas oil belong chiefly to the series C_nH_{2n-2}, containing a double polymethylene ring, whilst in Ohio oil members of the series C_nH_{2n+2}, C_nH_{2n}, and C_nH_{2n-4} are found. In Californian petroleums up to 15 per cent. of nitrogen compounds, containing 2 per cent. of nitrogen, are found, as also benzene, toluene, xylene, naphthalene, phenanthrene and anthracene. In the crude oil from the Santa Barbara County even members of the C_nH_{2n-8} series were found; this oil is remarkable for its high viscosity and specific gravity. The heavy Wietze oil is rich in asphalt. Engler and Jezioranski[1] showed that the fractions of Galician, Russian (Bibi-Eybat), and Pechelbronn oils boiling above

[1] *Ber.*, 1895, **28**, 2501.

200° dissolve almost completely in concentrated sulphuric acid, and contain on an average 87 per cent. of carbon (as against 85·7 per cent. in the olefines); hence they would appear to contain considerable quantities of more unsaturated hydrocarbons. In the case of Pennsylvanian petroleum, only 35 per cent. of the fractions boiling over 200° dissolve in concentrated sulphuric acid.

In the following Table the results obtained by the above authors are collated :—

Table I.

Crude oil from	C per cent.	H per cent.	O per cent.
Galicia	86·18	13·82	...
Baku.	86·21	13·49	0·30
Alsatia	85·38	12·68	1·94
Pennsylvania . . .	86·10	13·90	...

The fractions boiling below 200° contain principally saturated compounds of the methane and naphthene series. The elementary composition of crude oils from various sources varies within the following limits :—Carbon, 79·5-88·7; hydrogen, 9·6-14·8; oxygen, 0·1-6·9; nitrogen, 0·02-1·1; and sulphur, 0·01-2·2 per cent.

The following methods serve for the recognition and separation of the several groups of the constituents of petroleum :—

1. Acidic constituents (naphthenic acids, phenols) are extracted by dilute sodium hydroxide.

2. Nitrogen compounds (homologues of pyridine, etc.) are extracted by dilute mineral acid.

3. Unsaturated aliphatic hydrocarbons are extracted by sulphuric acid.

4. Aromatic hydrocarbons are detected by nitration.

5. Unsaturated cyclic hydrocarbons are separated by the Nastjukoff test (p. 86).

II. SPECIFIC GRAVITY AND COEFFICIENT OF EXPANSION.

The specific gravity of crude petroleum varies from 0·730-0·970; thus Pennsylvanian oil has a gravity of 0·816; Baku oil, 0·882; Ohio oil, 0·887; East Galician oil, 0·870; heavy Wietze oil, 0·955. In one case Engler found a sp. gr. of almost 1·0.

A low specific gravity indicates a high proportion of benzine and burning oil; a high specific gravity, on the other hand, indicates a notable proportion of high-boiling fractions and of asphalt. The specific gravity, although giving very little indication as to the source of a petroleum, may serve as a useful guide in the classification of oils of known origin, and has a considerable commercial importance for purposes of com-

parison and identification, inasmuch as the specific gravity forms the simplest means of controlling deliveries of oil.

The determination of the coefficient of expansion of crude oils is of importance for the correction of the specific gravity determined at various temperatures to the normal temperature ($15°$ or $20°$), as also for the calculation of the expansion of the oil in the storage vessels and stills.

The coefficient of expansion (a) of Pennsylvanian oil is 0·000840, that of Russian oil 0·000817 (of Wietze oil 0·000647); hence it decreases as the specific gravity rises. The values for a series of oils are given in the subjoined Table.

Table 2.

Source.	Sp. gr.	$a \times 1,000,000.$
Canada	0·828	843
Alsatia	0·829	843
„	0·861	858
West Galicia	0·885	775
Wallachia	0·901	748

Zaloziecki and Klarfeld found an exceptionally high coefficient of expansion (about 0·001) in the case of Galician crude oil from Boryslaw and Tustanowice.

The determination of the specific gravity and coefficient of expansion of crude oils is carried out as described in the section on "Lubricants" (this Vol., pp. 61 and 63).

III. DETERMINATION OF CONTAINED WATER.

1. A method much used in oil refineries, but not universally applicable, is to place a measured quantity of crude oil, say 200 c.c., in a 500 or 1000 c.c. stoppered cylinder, best constricted at the bottom and graduated. Two to four times the volume of petroleum spirit or of benzene are added, and the whole warmed and shaken. After settling, the water content is read off; but as emulsions are readily formed and the reading is thus rendered indistinct, it is usual to take only 70 per cent of the volume read off as water. The method of shaking with petroleum spirit is not applicable to oils which are rich in asphalt, as the latter is precipitated by petroleum spirit to some extent; in this case benzene must be used, which, however, readily leads to the formation of emulsions.

2. A method which is universally applicable for the determination of water consists in the distillation of the oil with xylene. According to Hofmann and J. Marcusson 100 g. of the crude oil (or 50 g. if the water content is high) are mixed with 100 c.c. of xylene, which has been

previously saturated with water by shaking, and distilled in a 600 c.c. flask containing fragments of pumice, until 80-90 c.c. have passed over. The distillate is collected in a graduated cylinder which is constricted at the bottom. After rinsing out the condenser tube with xylene, and detaching any drops of water adhering to the sides of the cylinder, the quantity of water can be read off.

M. Wielezynski[1] uses a centrifuge to separate the water, the centrifuge being heated by a steam-jacket in the case of thick oils. Mechanical impurities are, however, separated together with the water, and the separation is not always satisfactory. Other methods of a chemical character have been proposed, such as the alteration in the titre of $N/10$ hydrochloric acid on shaking with the oil, due to the dilution by the water present;[2] the measurement of the acetylene evolved when calcium carbide is allowed to react with the oil, and of the hydrogen evolved when sodium is brought into contact with an ethereal solution of the oil.[3] None of these proposals can be recommended.

IV. DETERMINATION OF MECHANICAL IMPURITIES.

Qualitative Examination.—Mechanical impurities are detected by shaking 2 c.c. of oil with 40 c.c. of benzene, and allowing to settle for several hours.

Quantitative Determination.—From 5-10 g. of the well-mixed oil are weighed out and dissolved in 100-200 c.c. of benzene. After standing for some time, any water which has separated out is drawn off, and the solution is filtered through a filter paper previously dried at 105°. After washing with benzene and drying at 105°, the filter paper and impurities are weighed.

Any suspended particles of pitch and asphaltic substances are not determined by this method, as they are dissolved by benzene; the determination of these is described on p. 9. Any mineral salts introduced by the bore-holes mud, or by chemicals added in the refining process, are determined by washing the residue on the filter with water, evaporating the solution, and weighing the residue.

Russian specifications direct to dilute a weighed quantity of the oil with petroleum spirit and to filter through a filter paper. The residue is incinerated and weighed.

V. YIELD OF NAPHTHA, BURNING OIL, LUBRICATING OIL, ETC.

Laboratory methods should be adapted to the requirements of the works concerned, the nature of the raw materials, the methods of distillation in use, and so forth. From one and the same crude oil very

[1] *Petroleum*, 1906, **2**, 285; cf. also Rosenthal, *Chem. Zeit.*, 1909, **33**, 1259.
[2] Nettel, *Chem. Zeit.*, 1904, **28**, 867.   [3] Graefe, *Petroleum*, 1906, **1**, 815.

different yields of the various fractions are obtained, depending on the method of distillation, the height of the fractionating column, and other factors. The general procedure in the laboratory consists in distilling from $\frac{1}{2}$ to 1 kg. of crude oil in glass or metal retorts. The distillate is condensed at first with water and then atmospherically, and is measured in definite ranges of boiling points up to 150° (*cf.* p. 17). The heavy fractions boiling above 300° are best distilled with superheated steam, in a vacuum of 300-400 mm. The characters of the distilled fractions are determined after purification by shaking with 1-8 per cent. of concentrated sulphuric acid.[1]

When mineral oils, after refining with acid, are washed with alkali and with water, persistent emulsions frequently make their appearance. Heavy oils must be kept hot and shaken violently to effect separation. As this is not easily done in a separating funnel, the washing and separating apparatus shown in Fig. 1 is recommended. The glass vessel *a*, having two stopcocks *d* and *d'* for emptying, is fitted with a glass or aluminium steam-coil *b*, and a glass tube *c* through which air is blown. The lower stopcock *d'* is useful for separating small quantities of oil which may have passed through *d*. Should the apparatus be used for refining
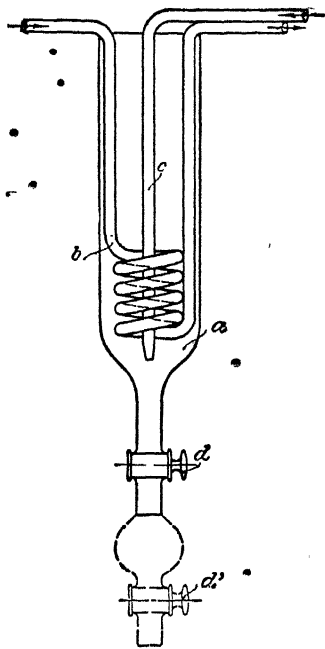
Fig. 1.

with acid, a third tap may be placed at the shoulder of the vessel, in order to separate the oil from resinous matter. The top of the vessel may be closed by a suitably bored lid to prevent splashing. Finally, the washed oil is dried by blowing the heated oil with air.

Since the various forms of laboratory distillation apparatus give quite discordant results with one and the same crude oil, specially constructed apparatus is employed for the fractional distillation of naphtha, kerosene, etc., for purposes of commercial control, and in Germany especially for Customs purposes.[2] These are made of specific dimensions, and give reliable comparative results under the same conditions of experiment.

Oils which contain water are carefully dehydrated before testing by shaking with calcium chloride at the ordinary temperature.

In place of the intermittent distillation by Engler's method,[3] which

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[1] *Cf.* Holde, *Mineralöle*, p. 16 *et seq.*   [2] *Cf.* Singer, *Chem. Rev.*, 1896, p. 93.
[3] *Cf.* Boverton Redwood, *Petroleum and its Products*, vol. ii., p. 204.

occupies a considerable time and does not always give concordant
results, the improved continuous distillation method of Holde and
Ubbelohde is to be recommended. The apparatus employed (Figs.
2, 3, 4) consists of the original Engler's flask (Fig. 2), which is heated
in a sheet-iron oven by a Bunsen burner fitted
with a tap. The condenser is 60 cm. long. The
distillate is collected in six test tubes divided
in 0.2 c.c. and rotatable in a stand. They are
cooled in water at the ordinary temperature.
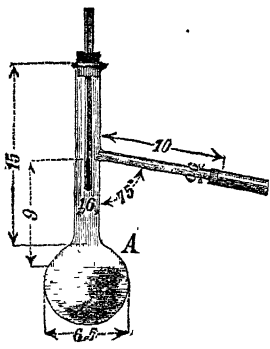
FIG. 2.

To carry out the test, 100 c.c. of oil are
filled into the distillation flask. This quantity
holds good, however, only for petroleum and
crude oils which yield a sufficient quantity of
low-boiling constituents in a given time, so
that the expansion of the heavy oils does not
cause any difficulty. For high-boiling oils, e.g.,
"astatki" and lubricating oils which would
readily boil over in a 100 c.c. flask, the flask must have a capacity of
at least 140 c.c., or the quantity of oil must be reduced to 80 or 90 c.c.
The temperature at which the first drops of distillate
fall into the receiver is taken as the boiling point.

The rate of boiling is fixed at 2 drops a second;
this is best controlled by means of a seconds'
pendulum.

In some factories, such as those working Gali-
cian oil, the boiling point limits of the petroleum
fraction are 150°-275°. All fractions except the last
are collected and measured without waiting for the
several fractions to drain off.

The fractional distillation test prescribed by the
New York Produce Exchange may be carried out
with a small still and condenser, or with any other
simple form of distilling apparatus. The fractions
taken off the condenser must each form one-tenth
of the crude oil by volume; the specific gravities of
each fraction must then be determined.

In Germany special apparatus is prescribed for
the use of Custom officers. The directions are laid
down in an official publication entitled, *Anleitung
für die Zollabfertigung*, Berlin, 1906, part iii.
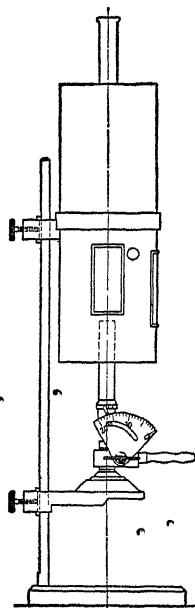
FIG. 3.

VI. FLASHING POINT.

The flashing point of an oil is the temperature at which it gives off
so much vapour, in the "open test," that the latter takes fire when a

flame is passed over the surface of the oil; or in the "close test," that temperature at which so much vapour collects above the surface of the oil in a closed vessel (Abel's, Gray's, or Pensky's apparatus) that it forms an inflammable mixture with the air contained in the vessel.

Crude oils from different sources have different flashing points, mostly in the neighbourhood of 0°. Those containing much naphtha, such as Javanese and American petroleum, have a considerably lower flashing point, whilst oils free from naphtha, such as the heavy Hanoverian oils, flash between 70° and 80°.
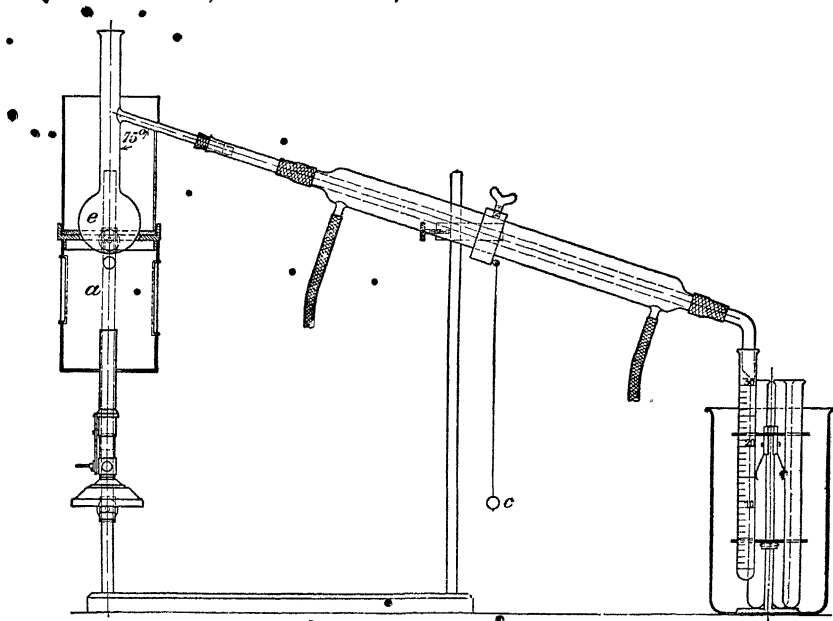
FIG. 4.

The flashing point is determined in this country by means of the standard Abel apparatus (see p. 29) in the case of low-flash oils, and by means of either the Pensky-Martens or Gray's apparatus in the case of high-flash oils. In Germany the Abel-Pensky and the Pensky-Martens apparatus are used for low-flash and high-flash oils respectively. At the recent International Petroleum Congress (Vienna, 1912), the Abel-Pensky (Abel-P.) apparatus was adopted as an international standard, provided, of course, it be sanctioned by legislation in the respective countries.[1]

VII. DETERMINATION OF ASPHALT.

Some crude petroleums (especially those of Hanover) contain notable amounts of asphalt. Analytical methods for its detection and

[1] Cf. *Petroleum*, 1912, **7**, 468.

quantitative estimation have been proposed by Holde. These methods, however, yield only comparative results, and therefore can be only looked upon as provisional, especially so as much depends on the character of the petroleum spirit employed for 'the extraction. In Germany a special "normal benzine" of the sp. gr. 0·695-0·705 at 15° and boiling from 65°-95° has been proposed for this purpose. (*Cf.* p. 21.)

Detection of Asphalt.—About 1 c.c. of crude oil is shaken in a test tube with 40 c.c. of petroleum spirit, and the liquid allowed to stand. If asphalt be present dark flocks separate out either immediately or on standing (for a day if necessary).

Or, 0·5 c.c. of oil is dissolved in 5 c.c. of ether, and 7 c.c. of alcohol are added. Hard and soft asphaltic substances are thereby precipitated, as a viscous mass adhering to the sides of the vessel.

Determination of Asphalt.

1. *Hard Asphalt.*—5 g. of crude oil are shaken in an Erlenmeyer flask with 220 c.c. of petroleum spirit; in the case of oils poor in asphalt, 5-20 c.c. of oil are taken. After standing for at least a day, the clear liquid is decanted through a small pleated filter. The bulk of the precipitate is brought on the filter, and the flask and filter are washed with the solvent until the filtrate no longer leaves an oily residue on evaporation. The asphalt on the filter is then dissolved by means of hot benzene, the solution concentrated by distillation, the remainder washed into a weighed dish, and the solid residue, after evaporation and drying at 100°, weighed. This procedure leaves any non-asphaltic matter which may have been precipitated by petroleum spirit on the filter; this may be estimated separately.

When it is desired to differentiate between dissolved and suspended asphalts in the crude oil, two determinations are made, as above— one on the original oil, the other on the same oil after it has been filtered without warming. The difference found represents suspended asphalt.

2. *Soft Asphalt.*—5 g. of crude oil are dissolved at 15° in 25 vols. of ether, and 12½ vols. of 96 per cent. alcohol are added, drop by drop, from a burette, with continuous shaking. After standing for five hours at 15°, the liquid is filtered as above, and the precipitate washed with ether-alcohol (2:1), so long as oily matter is extracted; it is then dissolved in benzene and evaporated down. In order to remove any paraffin wax in the residue, it is boiled out repeatedly with 30 c.c. of 96 per cent. alcohol, until no more paraffin wax separates out on cooling. Finally, the residue is dried for a quarter of an hour at 105°, and weighed.

VIII. PARAFFIN WAX.

1. A method of determining paraffin, originally proposed by Grotowsky, worked out by Engler and Bohm, and modified by Holde, is carried out as follows :—100 g. of crude petroleum are rapidly distilled from a glass retort until a thermometer placed in the vapours registers 300°. The condenser is then removed, a fresh receiver of known weight is fitted, and the remainder of the oil is distilled without a thermometer, until only coke is left behind. The weight of the heavy distillate, which is considered to contain all the paraffin wax, is then ascertained.

Of the heavy distillate, 5-10 g. are dissolved at the ordinary temperature in a mixture of equal volumes of absolute alcohol and ether. The solution is placed in a test tube (see Fig. 5) cooled to −20° until a clear solution results, and so much of the ether-alcohol mixture is added until, at −20°, all oily matter has disappeared, and only flocks of paraffin are observed. The paraffin wax is then filtered off by suction, in a funnel cooled by a freezing mixture (see Fig. 5), washed with previously cooled ether-alcohol, and finally washed off the filter with hot petroleum spirit or benzene into a weighed glass dish. After removal of the solvent by cautious evaporation on the water-bath, the outside of the dish is wiped dry, and its contents are examined. If the paraffin is hard, the dish is heated for a quarter of an hour at 105°, allowed to cool in a desiccator, and weighed. Should the paraffin, however, be soft, i.e., melting below 45°, it is better to dry it for several hours at 50° in a vacuum desiccator.
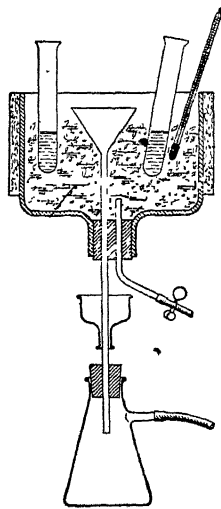
FIG. 5.

In washing the precipitated paraffin with cooled ether-alcohol, 5 c.c. of the filtrate must be tested from time to time by evaporation ; washing is complete when either the residue is negligible in amount or is solid at the ordinary temperature.

When the method is applied to crude paraffin waxes, 0·5-1 g. is weighed out and dissolved in 10-20 c.c. of ether-alcohol (see p. 46).

A correction is made for the solubility of paraffin wax in ether-alcohol. The percentage found is increased by 0·2 per cent. in the case of fluid oils, 0·4 per cent. in the case of oils beginning to solidify at 15°, and 1 per cent. in the case of crude paraffin wax.

This method gives the true proportion of paraffin only in the case of hard paraffin waxes suitable for candle-making. Soft paraffin waxes melting below 50° are not completely precipitated by ether-

alcohol at −20°; but the greater part of the paraffin which goes into solution can be recovered by evaporating down the filtrate, and redissolving the residue in the least possible quantity of ether-alcohol (1 : 2) at −20°. In the preliminary distillation (which is only necessary with the dark kinds of crude oil), a small proportion of paraffin wax undergoes decomposition. This source of error is the more serious, the higher the paraffin content of the crude oil; when there is 5 per cent. of paraffin present, the error may amount to 0·5 per cent. on the content of paraffin.

As the method described is universally applicable, other methods which have only a restricted application, need only be briefly mentioned.

2. B. Pawlewski and J. Filemonowicz[1] shake from 5-20 c.c. of oil with 100-200 c.c. of glacial acetic acid, filter off the separated paraffin, and wash it two or three times with glacial acetic acid and then two or three times with 75 per cent. alcohol, dry the precipitate, and weigh. The method does not, however, give reliable results for the paraffin wax in lignite or petroleum, as soft paraffin wax is soluble in glacial acetic acid, and heavy mineral oils cannot be separated quantitatively from paraffin wax by glacial acetic acid.

3. R. Zaloziecki[2] dissolves 10-20 c.c. of the sample in five times its volume of amyl alcohol, and precipitates with the same quantity of 75 per cent. ethyl alcohol at a temperature not exceeding 4°. After standing for several hours in the cold, the liquid is filtered through a cooled filter, and washed with a cooled mixture of 2 parts of amyl alcohol and 1 part of 70 per cent. alcohol. The paraffin wax is then dissolved in ether, and after evaporating this off, it is dried at 125° until the amyl alcohol is completely removed. This procedure may be used to determine paraffin wax in the presence of fatty acids, neutral fats, rosin and rosin oils, but cannot be used in the presence of beeswax, as this is also precipitated from amyl alcoholic solution by ethyl alcohol. Shukoff and Pantuchoff[3] subsequently suggested, as improvements on Zaloziecki's method, the use of 90 per cent. ethyl alcohol for the precipitation, and the cooling of all the solutions to 0°. The process is not suitable for mineral lubricants, especially those which are very viscous, as it is hardly possible to separate the paraffin wax completely from the oil. If, however, the precautions mentioned are carefully observed, it can be used with success for lignite-tar products. The drying of the paraffin wax at lower temperatures than 125° is recommended.

4. R. Höland's method[4] for the determination of paraffin wax in

[1] Ber., 1888, 21, 2973.
[2] Dingl. polyt. J., 1888, 269, 274 ; J. Soc. Chem. Ind., 1888, 7, 349.
[3] Russian "Journal of Fats," 1900.
[4] Chem. Zeit., 1893, 17, 1473, and 1483 ; J. Soc. Chem. Ind., 1894, 13, 286.

lignite-tar products has not been tested for other materials, and is probably unsuitable for petroleum products. It depends on the fact that the lignite-tar oils containing paraffin are soluble in absolute alcohol, and that at a certain temperature only the paraffin separates out.

IX. SPECIFIC HEAT.

The specific heat of crude oils is of importance, if it be a question of using the waste heat of steam for pre-heating the oil previous to distillation; or if dehydration of a crude oil by means of indirect steam is contemplated, when the amount of heating surface required can be calculated. The specific heat is also required for calculating the capacity of the refrigerating plant needed for the recovery of the paraffin wax.

Two methods are in use for the determination of the specific heat. E. Graefe[1] burns 0.41-0.43 g. of a substance of known heat of combustion (e.g. pure cellulose, in the form of absorbent pads, manufactured by Schleicher and Schüll; 1 kg. = 4175 Cal.) in a bomb calorimeter. The sample of oil is used as the outer liquid in the calorimeter. From the quantity of cellulose taken (a), the quantity of oil (b), the water equivalent of the calorimeter (W), and the observed rise of temperature (T), the specific heat can be calculated from the formula :—

$$a \cdot 4175 = W T + bc T.$$

By this method Graefe found the specific heat of various oils to range from 0.4-0.5.

Another method[2] depends upon the measurement of the heat produced by passing a current of known intensity (i) for a given time (z) through a strip of nichelin of resistance r immersed in the oil under examination. The rise of temperature (t) is read off, and the specific heat calculated from Joule's law (w being the water equivalent of the calorimeter), according to the formula :—

$$(m \cdot c + w) t = 0.239 i^2 r z.$$

The results obtained by this method in the "Reichsanstalt" are in good agreement with those of Graefe.

The more hydrogen an oil contains, the higher is its specific heat, and the richer it is in carbon and oxygen, the lower its specific heat. The specific heat as calculated from the elementary composition by Kopp's law, according to which the molecular heat equals the sum of the atomic heats, is in very good agreement with the experimental value. It is not even necessary to know the molecular composition

[1] *Petroleum*, 1907, 2, 521.
[2] *Cf.* Kohlrausch, *Introduction to Physical Measurements*, translated by Walter and Procter, 3rd ed., p. 118.

of the oil, as it is sufficient to divide the percentages of C, H, and O by the respective atomic weights, and to multiply these quotients by the atomic heats, viz., C = 1·8, H = 2·3, O = 4·0.

X. LATENT HEAT OF EVAPORATION OF PETROLEUM FRACTIONS.

A knowledge of these constants is necessary, in designing a works plant, for determining the requisite heating arrangements, the dimensions of the condensers, and the supply of condensing water. It is true that these data are commonly arrived at by empirical methods, but occasions arise when first principles have to be resorted to. The latent heats as required for the proper calculation of distilling and condensing plant may be conveniently determined in the apparatus designed by v. Syniewski,[1] shown in Fig. 6.
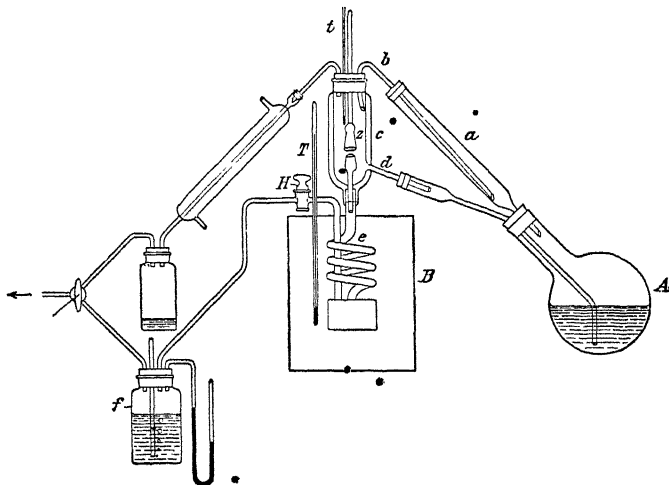
FIG. 6.

The vapour generated in the flask A, charged with about 400 c.c. of the fraction to be examined, passes through a b to the jacketed vessel c, and thence past the bell-valve z into the condensing worm e fitted inside the calorimeter B. The calorimeter system is closed off by z as long as condensation of vapour takes place in c, whence condensed liquid runs off through d. When c contains only vapour, free from liquid, z is opened and the vapour is admitted into the calorimeter, which is charged with about 1200 c.c. of water. The thermometers T and t serve to show the temperatures of the calorimeter and of the vapour respectively. Distillation into the calorimeter is continued until the boiling point has risen by 20°, it being convenient to deal with fractions at intervals of 20° boiling point. The calorimeter is now closed off at z and the whole of the distilling apparatus

[1] Z. angew. Chem., 1898, 11, 621 ; J. Soc. Chem. Ind., 1898, 17, 751.

removed, when the amount of condensed liquid is determined by weighing. The determination of the specific heat is conveniently carried out with the condensed liquid. The total heats of evaporation determined in this way at the " Reichsanstalt" ranged from 130-190 Cal. in the case of various crude oils and the products derived therefrom.

E. Graefe determines the heat of evaporation by passing the vapour of the mineral oil through a form of Liebig's condenser and measuring the rate of flow and rise of temperature of the condenser water, on the principle of the observations made with the Junkers' calorimeter. The loss of heat by radiation is determined in a preliminary experiment by distillation of a liquid of known heat of evaporation. The heats of evaporation of various lignite-tar oils were found to range from 120-220 Cal.

Graefe[1] has also shown that the heat of evaporation can be calculated from the molecular weight and the boiling points. Trouton had established for definite chemical compounds that when equimolecular quantities are taken, the quotient of the heat of evaporation and the absolute temperature of the boiling point is a constant, approximately 20. Now although the mineral oils are not definite chemical compounds, and moreover have not a constant boiling point, Trouton's formula can still be applied to them if mean values are adopted for the molecular weight and boiling point. The heat of evaporation is then :—

$$W = \frac{20\,T}{M}.$$

The mean molecular weight of an oil is determined by the lowering of the freezing point of commercial stearic acid. The molecular depression is ascertained in a preliminary experiment with a substance of known molecular weight; a weighed quantity (o) of the oil is then dissolved in a known quantity (s) of the stearic acid and the depression of the freezing point determined. If k be the molecular depression of the stearic acid and t the depression of the freezing point,

$$M = \frac{o.100.k}{s\,t}.$$

The following mean molecular weights were obtained in this way.

Table 3.

Lignite-tar oil.	Sp. gr.	Mol. wt.
Light crude oil	0·883	113
Heavy crude oil	0·905	158
Gas oil	0·890	158
Light paraffin oil	0·920	190

[1] *Petroleum*, 1910, 5, 569.

Charitschkoff,[1] by calculating the molecular weights from determinations of the vapour density by Hofmann's method, arrived at results similar to those of Graefe.

For the determination of the mean boiling point the oil is distilled continuously in Engler's apparatus, and the boiling points noted for each 10 per cent. The arithmetical mean of these temperatures gives the mean boiling point. Graefe found the following figures for a light crude oil. The liquid commenced to boil at 124°.

Distillate	10 p. c.	20 p. c.	30 p. c.	40 p. c.	50 p. c.
Temperature	173	184	192	201	210

Distillate	60 p. c.	70 p. c.	80 p. c.	90 p. c.	98 p. c.
Temperature	221	234	255	285	300

From this follows the mean boiling point = 216° C. = 489° abs. Using Trouton's formula, the heat of evaporation is :—

$$W = \frac{20T}{M} = \frac{204.89}{113} = 86.5.$$

In order to calculate the total heat of evaporation, the heat necessary to raise the oil from the ordinary temperature (25°) to the mean boiling point (216°) must be included. Taking the specific heat of the oil as 0.43, this gives 0.43 (216−25) = 82 Cal. Hence, the total heat of evaporation is 86.5 + 82 = 168.5 Cal. It is thus seen that in the case of this oil, almost as much heat is used in heating the oil to its boiling point as in the actual distillation. In many cases the conditions are still less favourable. From this result the great importance of warming the oil by waste heat before distilling is apparent.

B.—NAPHTHA.

The term "Naphtha," or "mineral naphtha," or "petroleum naphtha," is generally held to cover all those fractions of crude petroleum which boil below 150°. The limit of 150° is not observed by all refineries, and the naphthas sold are apt to show wide variations. The nature and value of both crude and redistilled naphtha are determined in the laboratory by fractional distillation with a dephlegmating apparatus.

In the commercial valuation of naphthas great stress is laid on a mild smell and on water-white colour. Patents have recently been taken out for masking the evil smell of badly refined naphtha by the admixture of turpentine and treatment with alkali. Such additions are detected by the methods given on p. 21.

[1] *Physikalische Untersuchung des Erdöls.*

I. SPECIFIC GRAVITY.

This is measured either by Mohr's balance, hydrometers, or pyknometers, and is stated for a temperature of 15° (see "Lubricants," p. 61). The specific gravity test serves chiefly for the identification of a sample.

The subjoined Table, due to Mendelejeff, facilitates the calculation of the specific gravity at the working temperature to that at the standard temperature of 15°:—

Table 4.

Sp. gr.	Correction for 1°.	
	Russian oil.	Pennsylvanian oil.
0·700 to 0·720	0·00082	0·00086
0·720 „ 0·740	0·00081	0·00082
0·740 „ 0·760	0·00080	0·00077
0·760 „ 0·780	0·00079	0·00072
0·780 „ 0·800	0·00078	0·00068

II. EVAPORATION TEST.

Petroleum spirit boiling below 100° (sp. gr. 0·70-0·71) should leave no residue when evaporated in a watch-glass on a lukewarm water-bath, nor should it leave a grease-spot on paper. A negative result with both of these tests indicates the certain absence of heavy oils.

III. FRACTIONAL DISTILLATION.

Petroleum spirit used as motor fuel should, according to Continental practice, contain nothing, or at very most 5 per cent., boiling above 100°. If this limit is exceeded, evaporation in the carburettor may become so sluggish, especially in cold weather, as to lead to misfires. Hence motor petrols, no less than solvent naphthas, need to be tested by fractionation. The commercial motor oils, sold in this country under the technical term "petrol," have higher boiling points; as a rule, 60-70 per cent. only boil below 100°, about 25 per cent. pass over between 100°-120°, 5-6 per cent. from 120°-133°, and about 3 per cent. above 133°.[1] Petrols containing much larger proportions of higher boiling fractions are, however, now used in modern carburettors in which the exhaust gases jacket the in-going air.

In the usual commercial distillation test 100 c.c. of naphtha are distilled directly from an Engler distilling flask, in the manner described

[1] *Cf.* B. Blount, "The Composition of Commercial Petrols," *The Incorporated Institution of Automobile Engineers*, 10th March, 1909 ; *J. Soc. Chem. Ind.*, 1909, **28**, 419.

on p. 6 for crude oil, and the fractions are collected for each interval
of 10°). The point at which the first drop of distillate falls from the
condenser is taken as the commencement of boiling, and the moment
at which the bottom of the distillation flask is just dry is taken as the
end point.

If the barometric pressure is not normal, this must be taken into
account in stating the boiling points and quantities of liquid in the suc-
cessive fractions.[1] The receiver is changed, in such a case, not exactly
at each round 10°, but at a slightly higher or lower temperature based
on the deviation of the boiling point of water from the normal at the
prevailing barometric pressure. R. Kissling has shown that this
correction is sufficiently accurate for all technical purposes. Such a
correction is to be applied whenever the atmospheric pressure deviates
by more than 5 mm. from 760 mm. To correct automatically for
differences of pressure, Fuss has suggested the use of a thermometer
with an adjustable scale, the 100° point being adjusted according to the
boiling point of water under the given barometric pressure; the ther-
mometer is divided into $\frac{1}{2}$ degrees, so that $\frac{1}{20}$ degrees can be estimated.

IV. FLASHING POINT.

As the vapour of petroleum naphtha (boiling as described above)
ignites well below 0°, the determination of the flashing point in the
Abel apparatus requires special precau-
tions, and should aim at keeping the
temperature well below freezing point.
The container of the Abel apparatus
(Fig. 7) is therefore placed in a cylindrical
metal pot b, about 60 mm. high and 90 mm.
wide, filled with alcohol. The pot is placed
in a larger vessel c, about 70 mm. high
and 160 mm. wide, also filled with alcohol,
and well insulated by felt. The cooling
below 0° is effected by introducing solid
carbonic acid into the alcohol as required.
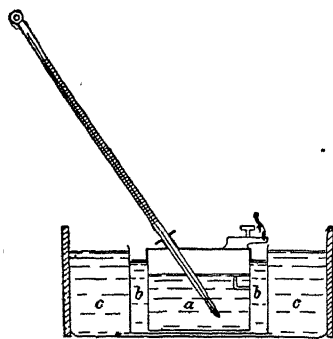
FIG. 7.

The ignition mechanism should be inserted, not from the beginning,
but immediately before the actual test commences; otherwise the flame
may go out during the test, owing to clogging of the wick by cold.
Moreover, the spring which governs the insertion of the ignition flame
is apt to work badly at low temperatures, and must be helped by
frequently turning the knob on the lid of the igniter. A temperature

[1] *Cf.* Ubbelohde, *Z. angew. Chem.*, 1906, **19**, 1155; and R. Kissling, *Chem. Zeit.*, 1908, **32**, 695.

of $-50°$ to $-60°$ having been reached, the container a is taken out bodily, and wrapped carefully in a cloth; the test is then carried out in the usual manner. After the flash test has been made, the ignition point may be determined; for this purpose the lid is taken off.

The following flashing points and ignition points of some naphtha fractions are given by Holde[1]:—

B.P.	50°-60°	60°-78°	70°-88°	80°-100°	80°-115°	100°-150°
Flashing point	below $-58°$	$-39°$	$-45°$	$-22°$	$-22°$	$+10°$
Ignition point	...	$-34°$	$-42°$	...	$-19°$	$+16°$

V. RISK OF EXPLOSION.

In gas engines, explosive mixtures of gas and air are purposely generated. It is to be borne in mind that combustible gases become explosive only when they are mixed with air, oxygen, or other gases which exercise an oxidising action. However, not every mixture of a combustible and an oxidising gas yields an explosive mixture, proper proportions of the two being required. Hence, there is a limited range of composition, within which explosion can occur. H. Bunte[2] has determined the explosive limits for various mixtures of air and gas (Table 5) in a gas-burette of 19 mm. diameter, the gas being ignited by a powerful electric spark.

Table 5.

Gas.	Percentage of combustible gas in the mixture.		
	No explosion.	Limits of explosion.	No explosion.
1. Carbon monoxide .	16·4	16·6 to 74·8	75·1
2. Water gas . .	12·3	12·5 ,, 66·6	66·9
3. Hydrogen . .	9·4	9·5 ,, 66·3	66·5
4. Acetylene . .	3·2	3·5 ,, 55·2	52·4
5. Coal gas . .	7·8	8·0 ,, 19·0	19·2
6. Ethylene . .	4·0	4·2 ,, 14·5	14·7
7. Alcohol . .	3·9	4·0 ,, 13·6	13·7
8. Methane . .	6·0	6·2 ,, 12·7	12·9
9. Ether . . .	2·6	2·9 ,, 7·5	7·9
10. Benzene . .	2·6	2·7 ,, 6·3	6·7
11. Pentane . .	2·3	2·5 ,, 4·8	5·0
12. Petroleum spirit .	2·3	2·5 ,, 4·8	5·0

These experiments were carried out under strictly comparable conditions, as the range of the limits of explosion depends not only on the nature of the gas, but also on the diameter of the tube, the method of ignition, the pressure, and the temperature. The influence of the last factor was determined in the case of carbon monoxide. Whereas

[1] *Mitt. k. Materialpruf.*, 1899, p. 70.   [2] *J. Gasbeleucht*, 1901, 44, 835.

the lower limit for this gas at the ordinary temperature is 16·6 per cent., it sinks to 14·2 per cent. at 400°, and to 7·4 per cent. at 600°.

It is seen from the Table that the limits of explosion for petroleum spirit lie very close together, the upper limit being only 5 per cent. of the vapour. On the other hand, it must not be overlooked that very small quantities of petroleum spirit are sufficient to cause an explosion.

It is advantageous, instead of employing Bunte's method of determination, to allow a certain quantity of vapour of petroleum spirit to evaporate into a gasometer holding a known volume of air, and then to draw the mixture into a Hempel explosion pipette over mercury for the ignition.

VI. HEAT OF COMBUSTION OF NAPHTHA (PETROL).

Since benzine has come into use for motors, especially for automobiles (cf. also p. 45), the determination of its heat of combustion has become of importance, as the value of an oil depends upon its calorimetric effect. The determination is carried out in a calorimetric bomb (Berthelot's, Mahler's, Kröcker's) placed in a water calorimeter, with a known quantity of oil and compressed pure oxygen, the ignition being effected electrically. The heat evolved by the combustion is measured by the rise in temperature of the calorimeter. The apparatus and the method of determination are described in the section on " Fuel," Vol. I., pp. 254 et seq.

The heats of combustion of benzine and burning oils are given in Table 6 in comparison with those of some other fuels.

Table 6.

Heating material.	Heat of combustion.
Naphtha	11,160 to 11,225
Petroleum	11,000 „ 11,100
Benzene	10,038
Motor Alcohol	5,940
Anthracite	8,000
Coal	7,000 to 7,500
Lignite (air-dry) . . .	4,500 „ 5,000

VII. AROMATIC HYDROCARBONS.

1. *Qualitative Detection.*—Asphalt, free from mineral matter, is finely powdered and thoroughly extracted with petroleum spirit of sp. gr.

0·70-0·71. A pinch of this is placed in a small filter, and the naphtha under examination is poured on to it. The filtrate is collected in a test tube; if it be colourless, benzene is absent, whereas if it show a yellow or brown tinge, the presence of benzene or toluene is indicated. This test, which is based on the solubility of asphalt in benzene, is sensitive enough to indicate an admixture of from 5-10 per cent. of aromatic hydrocarbons.

2. *Quantitative Determination.*—The method proposed by G. Krämer and W. Böttcher,[1] and based on the absorption of aromatic and olefinic hydrocarbons by sulphuric acid of sp. gr. 1·84 at 15° (prepared by mixing 20 vols. of fuming with 80 of ordinary concentrated acid), gives only approximately correct results.

VIII. OIL OF TURPENTINE (AMERICAN, RUSSIAN).

Oil of turpentine is best detected by determining the boiling point, the specific gravity, and the iodine value of the sample, or if need be of the fractions. American oil of turpentine yields 90 per cent. of distillate boiling from 155°-165°, has the sp. gr. 0·865 at 15°·5, and an iodine value of about 400.

Russian oil of turpentine ("Kienoel") yields 90 per cent. of distillate boiling from 160°-185°, has the sp. gr. 0·8610, and an iodine value of about 320. Benzine, on the other hand, has a much lower specific gravity and a very low iodine value [2] (if any).

IX. DEGREE OF PURIFICATION.

Commercial naphtha is more or less deep yellowish. Refined naphtha should be absolutely water-white, should impart no colour to concentrated sulphuric acid on shaking with it, and should yield no acid or other impurities to boiling distilled water.

X. SOLUBILITY IN ABSOLUTE ALCOHOL.

The naphtha fractions are completely soluble in absolute alcohol; naphtha is not miscible with 90 per cent. alcohol.

XI. PETROLEUM SPIRIT (NAPHTHA OR "NORMAL BENZINE").

As benzines used for the determination of "asphaltic substances" in dark mineral oils yield very different results according to their individual boiling points, the German "Verband für die Materialprüfungen der

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[1] *Gewerbefleiss*, 1887.
[2] *Cf.* Lewkowitsch, *Chem. Technology of Oils, Fats, and Waxes*, vol. iii., p. 125.

Technik" introduced in 1903 a "normal benzine" for these tests. This benzine is supplied solely by the firm of C. A. F. Kahlbaum, Berlin, under the control of the Royal Materialprüfungsamt at Gross-Lichterfelde near Berlin. This normal benzine must answer the following requirements :—

Sp. gr. at 15°, 0·695-0·705 ; extreme limits of boiling point 65°-95° (determined by continuous distillation from a small flask with a three-bulb Le Bel-Henninger fractionating column). It must not contain more than 2 per cent. of substances which dissolve in a mixture of 80 parts of concentrated and 20 parts of fuming sulphuric acid.

XII. PETROLEUM SPIRIT FOR VARNISHES AND OIL OF TURPENTINE SUBSTITUTES.

The identification of pure oil of turpentine substitutes, such as "Kienöl" (see above, p. 21), perchlorethylene, etc., presents no analytical difficulties.[1]

The substitutes used in the manufacture of varnishes, sold in this country as "White Spirit," have, as a rule, a flashing point above 23° (73° F.), mostly at 26°·7 (80° F.); evaporate as nearly as possible at the same rate as does genuine oil of turpentine, yield 90 per cent. of distillate up to 140°, have a sp. gr. of about 0·785, and are characterised by a mild odour.

The rate of evaporation is determined by a comparative test with pure oil of turpentine, the liquids being evaporated in a platinum dish on a boiling water-bath. Pure oil of turpentine may leave from 1·5-2 per cent. of a solid residue ; the substitute, however, should leave no residue. A convenient comparative test, which can be carried out in the cold, is to moisten a strip of filter paper with an equal number of drops of turpentine and the benzine under examination, and to observe the time which elapses before the liquid has evaporated off completely.

Many quantitative methods have been proposed for the determination of benzine in turpentine substitutes,[2] but these have all been rejected on account of inaccuracy. The method which has proved itself the best is J. Marcusson's [3] modification of Burton's method, in which fuming nitric acid is allowed to act on 10 c.c. of the oil at −10°. Turpentine and "Kienöle" pass completely into solution under this treatment, or give at most 1·5 per cent. of precipitate. A defect in the original method was that certain components of the benzines, viz.,

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[1] Cf. Lewkowitsch, loc. cit.

[2] Cf. H. E. Armstrong, J. Soc. Chem. Ind., 1882, 1, 478 ; Richardson and Bowen, J. Soc. Chem. Ind., 1908, 27, 613 ; Burton, Amer. Chem. J., 1890, 12, 102 ; Allen, Chem. Zentr., 1890, II., 125.

[3] Mitteilungen, 1908, p. 157 ; J. Soc. Chem. Ind., 1909, 28, 1096.

aromatic and olefinic hydrocarbons, also pass into solution, giving rise to low results in the determination of the benzines. In the subjoined Table a series of results obtained by this method for oil of turpentine mixed with Galician and Sumatra benzines are given.

Table 7.

Source of benzine used	Percentage of benzine.	Insol. in nitric acid.	Extract from nitric acid solution (freed from acid).			Benzine content found.	Difference between found and true.
		Per cent.	g.	c.c.	Per cent. on original oil.	Per cent.	Percentage.
Sumatra (heavy) .	80	49·0	3·82	3·32	33·2	82·2	+2·2
,, (light) .	80	57·5	2·40	2·10	21·0	78·5	−1·5
,, (heavy) .	60	33·0	2·80	2·44	24·4	57·4	−2·6
Galicia . . .	40	30·0	1·02	0·90	9·0	39·0	−1·0
,, . . .	20	11·0	1·03	0·90	9·0	20·0	±0·0
Sumatra (heavy) .	10	4·0	0·79	0·70	7·0	11·0	+1·0

Marcusson's method also gives valuable information as to the source of the benzine present. If the range of boiling point is 100°-180° and the specific gravity of the portion insoluble in nitric acid is 0·72-0·73, the benzine is probably of American origin; a specific gravity of 0·74-0·75 indicates Galician or Roumanian benzine; 0·76-0·77, Indian; 0·78, Russian. A second criterion is the content of substances soluble in nitric acid. Taking, as before, a boiling point from 100°-180°, the percentage of soluble matter calculated on the total benzine is, in the case of American and Russian benzines, 8-10 per cent.; in Galician and Roumanian, 15-20 per cent.; in Indian, 2a-40 per cent.

A modification of Armstrong's polymerisation method for this estimation has been recently recommended by R. S. Morrell.[1]

C.—BURNING OIL (KEROSENE).

I. COLOUR.

Good burning oil (Kerosene, paraffin oil, etc.) boiling between 150° and 300° and prepared by treating the crude oil with sulphuric acid, should be clear, transparent, and, at most, of a faintly yellow tint. The higher grades, such as "water-white," are colourless. On exposure to sunlight all burning oils become slightly discoloured, without however suffering to any extent in their illuminating properties. For commercial purposes burning oil is classified according to colour. Standardising

colorimeters, which enable the grade of an oil to be determined, have been devised by A. Wilson, and by C. Stammer.

1. *Wilson's Colorimeter* consists of a box, the lid of which may be clamped at any angle and acts as a stand for two brass tubes *b* (Figs. 8 and 9), 16 in. long, holding the oil and the standard glasses respectively. Both tubes are closed by thin glass plates fixed in screw-caps. A mirror at the bottom of the lid reflects the light through the tubes and through a pair of prisms into the eye-piece. The field, as seen through the eye-piece, is divided by a sharp line which allows of the comparison of the two halves of the field, which are tinted respectively with the colour of the oil and that of the standard. A series of four standard glasses is supplied with each colorimeter, corresponding, in ascending order of depth, to the four commercial grades — water-white, superfine white, prime white, and standard white.
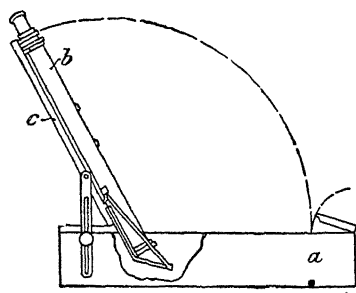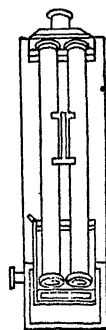
FIG. 8.   FIG. 9.

In making a determination, one of the tubes is filled with oil, the other remaining empty. The tubes are first fixed in position; one-half of the field seen through the eye-piece will now, of course, be darker than the other. Standard glasses are then inserted in the empty tube, until both halves of the field have approximately the same tint. The grade of the oil is thus fixed.

It is very rare that an oil corresponds exactly to one of the standard glasses. Since, however, these are the only recognised standards, if the colour of an oil should lie between say No. 2 and No. 3 standard, the oil is classified according to the darker tint, *i.e.* as No. 3. In Baku the common practice is to express the grade in fractions of the standard number.

The colour of the burning oil manufactured at Baku generally lies between the standard numbers 2 and 3. Intermediate fractions are determined as follows:—Standard glass No. 2 is placed over the tube containing the oil, and No. 3 over the empty tube. If the two halves of the field be found to be equalised, then the grade of the oil is $2\frac{1}{2}$.

If under these conditions the oil appears too dark, the grade $2\frac{3}{4}$ is assigned to it; if too light, the grade $2\frac{1}{4}$. Again if glass No. 1 on the filled tube compensates No. 3 on the empty one, the oil is graded as No. $2\frac{1}{4}$.

2. *Stammer's Colorimeter.*—This instrument has the advantage over that of Wilson that it allows of the variation of the length of the column of oil measured, whereby the shade of colour can be more accurately defined. It is largely used at Baku.

The construction of the apparatus is shown diagrammatically in Fig. 10. A fixed tube z, on which is placed a standard glass plate u is arranged side by side with a cylinder c in which the oil is placed; this cylinder can be moved up and down by means of the hand-wheel k, whereby the length of the column of oil under comparison is varied at will. Both z and c are closed at the bottom by thin glass plates through which the light reflected from the mirror p reaches the eye-piece o. The length of the column of oil is adjusted until both fields, as seen through the eye-piece, have the same depth of tint, and this length is measured on the scale m.

The use of the single glass standard was found by Boverton Redwood[1] to be open to objection, as the sensitiveness of the test was much impaired in cases in which the column of oil had to be greatly shortened for the com-

Fig. 10.

parison. Modifications introduced by R. Redwood have overcome this defect. The space between any two of the four commercial shades is divided into ten equal parts, so that if the colour, for instance, of a sample is midway between "water-white" and "superfine white" it would be indicated by the figure 1·5.

The following Table gives the relations between grade number by Wilson's colorimeter, and height of column in Stammer's colorimeter. The figures in the third column, in the case of whole grade numbers, were arrived at by direct experiment, and in the case of the remaining numbers, by calculation.

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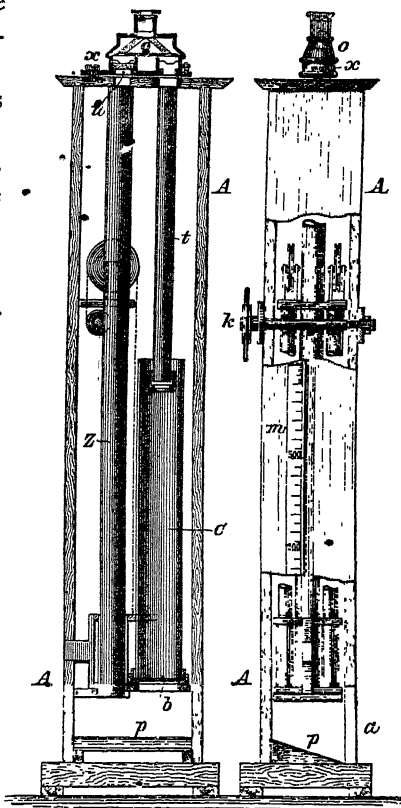
[1] Cf. *Petroleum and its Products*, 3rd ed., 1913, vol. ii., p. 215.

Standard white	. No. 4	50	mm.	Prime white .	. No. $2\frac{1}{4}$	172	mm.
,, . .	. ,, $3\frac{1}{2}$	68	,,	Superfine white	. ,, 2	199	,,
Prime white .	. ,, 3	86·5	,,	,, .	. ,, $1\frac{1}{2}$	255	,,
· ,, .	. ,, $2\frac{3}{4}$	115	,,	Water-white .	. ,, 1	310	,,
,, .	. ,, $2\frac{1}{2}$	143	,,				

According to the rules of the Baku section of the Imperial Russian Technical Society, the colour of a burning oil is by no means the only factor determining its degree of purity or its behaviour in burning. As, however, burning oil is bought and sold very largely on a basis of colour, it was regarded as desirable to standarise the colorimetric tests employed. Since the tints of the standard glasses in the above-described colorimeters are found to vary a little, a minute comparison of grades, Wilson numbers, and Stammer columns, was made by the Baku section with a readily reproducible standard, viz., potassium chromate dissolved in acidulated water in a column 404·6 mm. high. The results of these tests are given in the following Table :—

<div align="center">Table 8.</div>

Grade.	Number.	Percentage strength of K_2CrO_4 solution.	Column of oil in mm.
Water-white . .	1·0	·000272	957·9
,,	1·1	·000309	843·2
,,	1·2	·000346	753·1
,,	1·3	·000384	680·3
,,	1·4	·000421	618·9
,,	1·5	·000458	568·4
,,	1·6	·000495	526·4
,,	1·7	·000532	489·8
,,	1·8	·000570	557·1
,, .	1·9	·000607	429·3
Superfine white .	2·0	·000644	404·6
,,	2·1	·000886	294·1
,,	2·2	·001129	230·8
,,	2·25	·001220	208·5
,,	2·3	·001371	191·1
,,	2·4	·001614	161·4
,,	2·5	·001856	140·4
,, .	2·6	·002098	124·2
,,	2·7	·002341	111·3
,,	2·75	·002462	105·8
,,	2·8	·002583	100·9
,, .	2·9	·002826	92·2
Prime white .	3·0	·003068	84·9
,,	3·1	·003325	78·4
,,	3·2	·003581	72·8
,,	3·3	·003838	67·9
,,	3·4	·004094	63·6
,,	3·5	·004351	59·9
,,	3·6	·004608	56·5
,,	3·7	·004864	53·5
,, .	3·8	·005121	50·9
,, .	3·9	·005377	48·5
Standard white .	4·0	·005634	46·2

It will be observed that the scale of solutions of potassium chromate is so designed that each interval between two standard commercial grades is divided into tenths. Thus the difference for each unit

is ·000037 per cent. chromate between water-white and superfine white, ·0000242 per cent. between superfine white and prime white, and so on. The colour of any given oil can be stated in terms of this scale by comparing it in a Stammer colorimeter with a standardised glass having the tint of a 404·6 mm. column of superfine white oil. Superfine white is the most suitable standard, because with it the inevitable qualitative differences of colour are reduced to a minimum. An oil paler than superfine white must be compared with a water-white glass, since columns longer than 404·6 mm. cannot be examined.

When comparison is made with a glass corresponding to water-white, the following Table gives the requisite data :—

Table 9.

Grade.	Number.	Percentage strength of K_2CrO_4 solution.	Column of oil in mm.
Water-white . .	1·0	·000272	404·6
,, . .	1·1	·000309	356·2
,, . .	1·2	·000346	318·1
,, . .	1·3	·000384	286·6
,, . .	1·4	·000421	261·4
,, . .	1·5	·000458	240·3
,, . .	1·6	·000495	222·3
,, . .	1·7	·000532	206·9
,, . .	1·8	·000570	193·1
,, . .	1·9	·000607	181·3
Superfine white .	2·0	·000644	170·9

Colorimeter glasses which have not quite the correct standard colour are themselves standardised by comparison with potassium chromate solutions. The amount of divergence having been ascertained, the proper correction is applied in the fourth column of the Tables, when such a glass is used.

II. SPECIFIC GRAVITY.

The specific gravity is, as a rule, expressed for a temperature of 15° compared with water at 4°.

The corrections to be applied for temperatures differing from 15° are given in the following Table prepared by Mendelejeff :—

Table 10.

Range of sp. gr.	Correction for 1°.
0·760 to 0·780	·000790
0·780 ,, 0·800	·000780
0·800 ,, 0·810	·000770
0·810 ,, 0·820	·000760
0·820 ,, 0·830	·000750
0·830 ,, 0·840	·000740
0·840 ,, 0·850	·000720
0·850 ,, 0·860	·000710

Petroleum increases perceptibly in specific gravity on keeping for a long time, even in stoppered bottles; Engler[1] ascribes this as being due to polymerisation.

III. VISCOSITY.

This, if required, may be determined by means of Redwood's viscometer, which is fully described in the section on "Lubricating Oils" (p. 66).

IV. SOLIDIFYING POINT.

Burning oils, if likely to be used in open places, must remain liquid below the freezing point of water. The test is carried out as described in the section on "Lubricants" (p. 70).

American petroleum separates particles of paraffin at − 10° unless it has been carefully distilled, whereas Russian petroleum remains perfectly clear at − 20°.

V. FLASHING POINT.

The flashing point of a mineral oil is that temperature at which it begins to evolve inflammable vapour in sufficient quantity for a momentary "flash" to occur on the application of a flame. The testing of the flashing point as a safeguard against the presence of very volatile hydrocarbons in burning oils has been made the basis of legislation in regard to petroleum. The test is an arbitrary one, and various forms of instruments have been adopted in different countries for legislative purposes.

The first Petroleum Act in this country was passed in 1862, but remained practically inoperative, as no method of testing was prescribed. Subsequent Acts were passed in 1868 and 1871, in which an "open test" was prescribed. Petroleum was defined for the purposes of these Acts as "any Rock oil, Rangoon oil, Burma oil, oil made from petroleum, coal, schist, shale, peat, or other bituminous substance, or any products of petroleum, or any of the above-mentioned oils which gives off an inflammable vapour at a temperature of less than 100° F." In 1879 a further Petroleum Act was passed, as the result of investigations by Sir Frederick Abel, in which the "closed test," now known as the Abel test, was adopted. The result of a large number of experiments on the difference between the flashing points with the open-cup instrument and with Abel's closed tester gave a mean value of 27° F., in accordance with which the new standard of temperature was fixed at 73° F. (22°·8 C.). This Act of 1879, in conjunction with that of 1871, is still in force. The specification of the test apparatus and the details for applying the test are given below. Every apparatus in use for official purposes must be standardised by the Board of Trade.

The Abel Petroleum Test Apparatus.

Specification of the Test Apparatus.—The following is a description of the details of the apparatus, Fig. 11 :—The oil cup consists of a cylindrical vessel 2 in. diameter, $2\frac{2}{10}$ in. height (internal), with outward projecting rim $\frac{5}{10}$ in. wide, $\frac{3}{8}$ in. from the top, and $1\frac{7}{8}$ in. from the bottom of the cup. It is made of gun metal or brass (17 B.W.G.) tinned inside. A bracket, consisting of a short stout piece of wire bent upwards and terminating in a point, is fixed to the inside of the cup to serve as a gauge. The distance of the point from the bottom of the cup is $1\frac{1}{2}$ in. The cup is provided with a close-fitting overlapping cover made of brass (22 B.W.G.), which carries the thermometer and test lamp. The latter is suspended from two supports from the side by means of trunnions upon which it may be made to oscillate; it is provided with a spout, the mouth of which is $\frac{1}{10}$ in. in diameter. The socket which is to hold the thermometer is fixed at such an angle and its length is so adjusted that the bulb of the thermometer when inserted to its full depth shall be $1\frac{1}{2}$ in. below the centre of the lid.

The cover is provided with three square holes, one in the centre, $\frac{5}{10}$ in. by $\frac{4}{10}$ in., and two smaller ones, $\frac{3}{10}$ in. by $\frac{2}{10}$ in., close to the sides and opposite each other. These three holes may be closed and uncovered by means of a slide moving in grooves, and having perforations corresponding to those on the lid.

In moving the slide so as to uncover the holes, the oscillating lamp is caught by a pin fixed in the slide, and tilted in such a way as to bring the end of the spout just below the surface of the lid. Upon the slide being pushed back so as to cover the holes, the lamp returns to its original position.

Fig. 11.

Upon the cover, in front of and in line with the mouth of the lamp, is fixed a white bead, the dimensions of which represent the size of the test flame to be used.

The bath or heated vessel consists of two flat-bottomed copper cylinders (24 B.W.G.), an inner one of 3 in. diameter and $2\frac{1}{2}$ in. height,
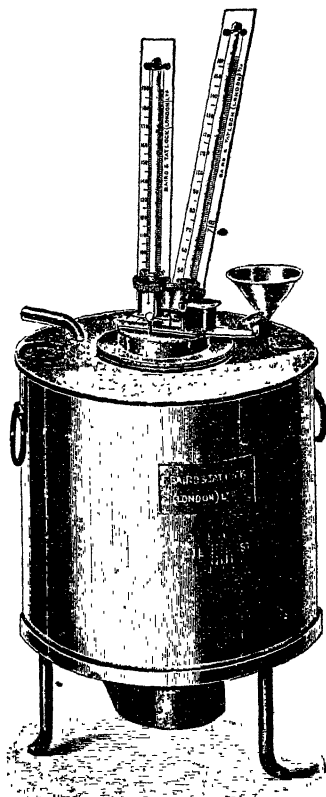
and an outer one of $5\frac{1}{2}$ in. diameter and $5\frac{3}{4}$ in. height; they are soldered to a circular copper plate (20 B.W.G.) perforated in the centre, which forms the top of the bath, in such a manner as to enclose the space between the two cylinders, but leaving access to the inner cylinder. The top of the bath projects both outwards and inwards about $\frac{3}{8}$ in.; that is, its diameter is about $\frac{3}{4}$ in. greater than that of the body of the bath, while the diameter of the circular opening in the centre is about the same amount less than that of the inner copper cylinder. To the inner projection of the top is fastened, by six small screws, a flat ring of ebonite, the screws being sunk below the surface of the ebonite, to avoid metallic contact between the bath and the oil cup. The exact distance between the sides and bottom of the bath and of the oil lamp is one-half of an inch. A split socket similar to that on the cover of the oil cup, but set at a right angle, allows a thermometer to be inserted into the space between the two cylinders. The bath is further provided with a funnel, an overflow pipe, and two loop handles.

The bath rests upon a cast-iron tripod stand, to the ring of which is attached a copper cylinder or jacket (24 B.W.G.) flanged at the top, and of such dimensions that the bath, while firmly resting on the iron ring, just touches with its projecting top the inward-turned flange. The diameter of this outer jacket is $6\frac{1}{2}$ in. One of the three legs of the stand serves as support for the spirit lamp attached to it by means of a small swing bracket. The distance of the wick holder from the bottom of the bath is 1 in.

Two thermometers are provided with the apparatus, the one for ascertaining the temperature of the bath, the other for determining the flashing point. The thermometer for ascertaining the temperature of the water has a long bulb and a space at the top. Its range is from about $90°$-$190°$ F. The scale (in degrees Fahrenheit) is marked on an ivory back fastened to the tube in the usual way. It is fitted with a metal collar, fitting the socket, and the part of the tube below the scale should have a length of about $3\frac{1}{2}$ in. measured from the lower end of the scale to the end of the bulb. The thermometer for ascertaining the temperature of the oil is fitted with a collar and ivory scale in a similar manner to the one described. It has a round bulb, a space at the top, and ranges from about $55°$-$150°$ F.; it measures from end of ivory back to bulb $2\frac{1}{4}$ in.

NOTE.—A model apparatus is deposited at the Weights and Measures Department of the Board of Trade.

Directions for applying the Flashing Test.—1. The test apparatus is to be placed for use in a position where it is not exposed to currents of air or draughts.

2. The heating vessel or water-bath is filled by pouring water into the funnel until it begins to flow out at the spout of the vessel. The

temperature of the water at the commencement of the test is to be 130° F., and this is attained in the first instance either by mixing hot and cold water in the bath, or in a vessel from which the bath is filled, until the thermometer which is provided for testing the temperature of the water gives the proper indication; or by heating the water with the spirit lamp (which is attached to the stand of the apparatus) until the required temperature is indicated.

If the water has been heated too highly, it is easily reduced to 130° F. by pouring in cold water, little by little (to replace a portion of the warm water), until the thermometer gives the proper reading.

When a test has been completed, this water-bath is again raised to 130° F. by placing the lamp underneath, and the result is readily obtained while the petroleum cup is being emptied, cooled, and refilled with a fresh sample to be tested. The lamp is then turned on its swivel from under the apparatus, and the next test is proceeded with.

3. The test lamp is prepared for use by fitting it with a piece of flat plaited candle wick, and filling it with colza or rape oil up to the lower edge of the opening of the spout or wick tube. The lamp is trimmed so that when lighted it gives a flame of about 0·15 in. diameter, and this size of flame, which is represented by the projecting white bead on the cover of the oil cup, is readily maintained by simple manipulation from time to time with a small wire trimmer.

When gas is available it may be conveniently used in place of the little oil lamp, and for this purpose a test-flame arrangement for use with gas may be substituted for the lamp.

4. The bath having been raised to the proper temperature, the oil to be tested is introduced into the petroleum cup, being poured in slowly until the level of the liquid just reaches the point of the gauge which is fixed in the cup. In warm weather the temperature of the room in which the samples to be tested have been kept should be observed in the first instance, and if it exceeds 65.° F. the samples to be tested should be cooled down (to about 60° F.) by immersing the bottles containing them in cold water, or by any other convenient method. The lid of the cup, with the slide closed, is then put on, and the cup is placed into the bath or heating vessel. The thermometer in the lid of the cup has been adjusted so as to have its bulb just immersed in the liquid, and its position is not under any circumstances to be altered. When the cup has been placed in the proper position, the scale of the thermometer faces the operator.

5. The test lamp is then placed in position upon the lid of the cup, the lead line or pendulum, which has been fixed in a convenient position in front of the operator, is set in motion, and the rise of the thermometer in the petroleum cup is watched. When the temperature has reached about 66° F. the operation of testing is to be commenced,

the test flame being applied once for every rise of one degree, in the following manner:—

The slide is slowly drawn open while the pendulum performs three oscillations, and is closed during the fourth oscillation.

NOTE.—If it is desired to employ the test apparatus to determine the flashing points of oil of very low volatility, the mode of proceeding is to be modified as follows:—

The air chamber which surrounds the cup is filled with cold water to a depth of $1\frac{1}{2}$ in., and the heating vessel or water-bath is filled as usual, but also with cold water. The lamp is then placed under the apparatus and kept there during the entire operation. If a very heavy oil is being dealt with the operation may be commenced with water previously heated to 120°, instead of with cold water.
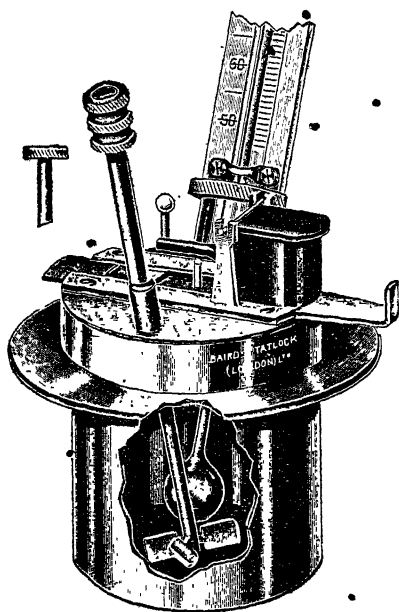
Effects of Variation in Barometric Pressure.—The results obtained with the Abel apparatus vary with the barometric pressure, the difference in the flashing point amounting to 0°·636 F. (0°·30 C.) for each 10 mm. difference in pressure. A Table of corrections, given on p. 37, is in use in Germany in connection with the Abel-Pensky instrument; no corrections are prescribed by the Petroleum Act in this country.

FIG. 12.

Effect of a Tropical Climate.—The effect of a tropical climate on the liberation of vapour causes a lowering of the flashing point. Investigations by F. Abel and Boverton Redwood[1] have shown that this source of error in the determination of the flashing point may be overcome by commencing the test many degrees below the flashing point, so that the vapour is withdrawn by the current of air created by the test flame, in successive quantities too small to cause a flash before volatilisation of the oil begins. With this modification, which is embodied in the Indian Petroleum Act, 1899 (as modified to 1st Nov. 1903), the results obtained at a tropical temperature agree very closely with those obtained in a temperate climate.[2] The Act prescribes the Pensky modification of the Abel apparatus (p. 33) for carrying out the test.

[1] *Chem. News*, 1884, **49**, 196.
[2] *Cf.* Redwood, *Petroleum and its Products*, vol. ii., pp. 231-238.

Petroleum Mixtures.—Since mixtures of petroleum with other substances present similar dangers to petroleum without admixture, an Order in Council[1] was introduced in 1907 in regard to such mixtures. The prescribed apparatus (Fig. 12) differs from the Abel apparatus described above in the addition of a stirrer, to equalise the temperature throughout the sample during the test, and must be used for all viscous and sedimentary mixtures.

The Abel-Pensky Petroleum Test Apparatus.

This modification of the Abel apparatus is provided with a clock-work arrangement for the removal of the slide and the application of the
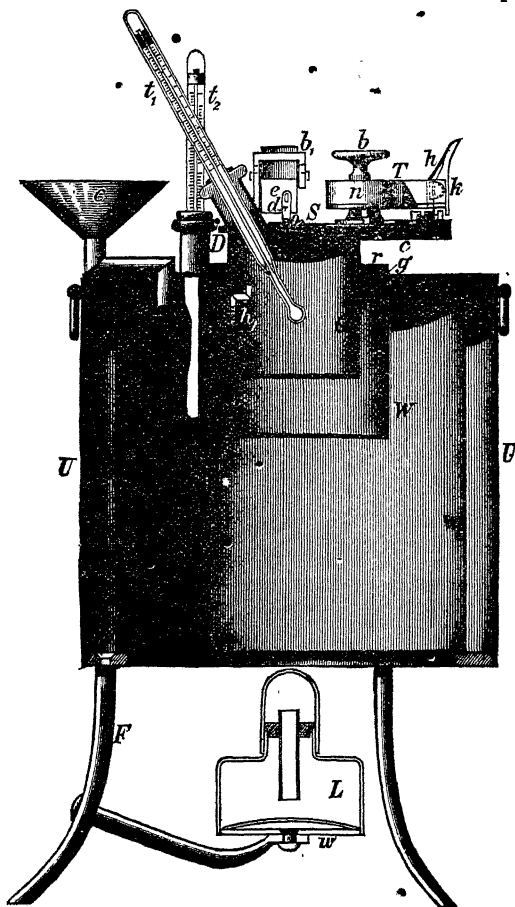
FIG. 13.

test-flame, whereby greater uniformity is secured in the tests and the liability to the personal error introduced by the method of applying the

III   C

test-flame is considerably reduced. It has been adopted as the standard instrument for legislative purposes in Germany, Russia, and in India.

The apparatus (Fig. 13) consists of a water-bath W, an oil-container G, a lid fitted with a thermometer, and an igniting device, operated by a special mechanism. In the lid of the water-bath are fixed a funnel C, an exit-pipe (not shown in the figure), and a thermometer t_2. A hollow copper vessel dips into the water-bath. This acts as an air-jacket to the container, and has an ebonite-lined neck. The container G, which fits into this neck, is tinned internally and provided with a grip h_1, up to the level of which it is filled with the oil to be tested. The lid of G carries a thermometer t_1, and on it lies the flat metal slide-valve S, which is actuated by the clockwork mechanism T, and is pierced with a series of holes corresponding with holes in the lid of G; at one end of the stroke G is thus closed off, and at the other end it communicates with the open air through the holes referred to.

To set the clockwork in action, the screw b is turned to the right as far as it will go. On depressing the lever h, the slide-valve is set in motion. At the same time the small lamp a, which oscillates on a horizontal swivel, is made to dip downwards; the lamp has a spout d, which carries a wick at which a tiny flame is kept burning. Matters are so adjusted that this flame dips into the upper part of G (which contains a mixture of oil vapours and air) for two seconds at the point where the openings of the slide-valve are over the openings of G.

To determine the flashing point the oil is introduced into the container by means of a pipette, and is cooled, before the ignition mechanism is brought into play, to 2° below the lowest possible limit of the flashing point. The initial adjustment of temperature is effected before G is placed in the water-bath. Care should be taken that no oil lodges on the inside of G above the level of h.

The relation between the barometric pressure and the temperature at which testing should begin is shown by the following Table :—

Table II.

Barometric pressure.	Initial temperature.
From 685 to 695 mm.	+14·0° C.
Above 695 ,, 705 ,,	14·5
,, 705 ,, 715 ,,	15·0
,, 715 ,, 725 ,,	15·5
,, 725 ,, 735 ,,	16·0
,, 735 ,, 745 ,,	16·0
,, 745 ,, 755 ,,	16·5
,, 755 ,, 765 ,,	17·0
,, 765 ,, 775 ,,	17·0
,, 775 ,, 785 ,,	17·5

The ignition flame, which is fed, through a cotton wick, from the petroleum reservoir $d\,e$, is lighted when the temperature of the water-bath has reached 54°-55° C. (129°-131° F.), and is set in motion by winding up b and depressing h; at the same time the spirit lamp L is extinguished. The test is made at $\frac{1}{2}$° intervals. A white bead let into the lid of the tester indicates the size to which the flame should be adjusted.

As the flashing point is approached, the ignition flame is observed to grow larger through the formation of a halo of light surrounding it. The true flashing point, however, is not reached until a momentary blue flame plays over the whole empty space above the oil. A further condition is that the ignition flame shall not be blown out by this occurrence, as often happens in the first flashings. The temperature at which definite flashing sets in is read off at the thermometer t_1.

The test is repeated with a fresh portion of the oil, and if the result of the second test does not differ by more than 0°·5 from the first, the mean of the two temperatures is taken as the flashing point; should the two readings differ by 1° or more, a third test is made, and if the maximum difference between the three readings does not exceed 1°·5, the average is taken.

The minimum flashing point prescribed in Germany is 21° C. (69°·8 F.) at 760 mm. pressure. The apparent flashing points must be corrected for pressure in accordance with Table 12 (p. 37), in which flashing points from 15°·5-25°·9 are tabulated under pressures from 650-785 mm.; the flashing points at the normal pressure are given in the column between the two thick lines, and the corresponding flashing points at other pressures are given in the same horizontal line.

Other Apparatus for testing the Flashing Point of Petroleum.

Several other forms of apparatus have been devised for testing the flashing point of petroleum.

In the State of New York an apparatus devised by A. H. Elliot is prescribed for legal purposes, whilst in many of the other States of the American Union the Tagliabue closed tester or cup has been adopted. In France, Granier's automatic tester is employed officially. A full description of these instruments together with directions for their use and the legislative conditions governing the testing, storage, transport, and use of petroleum and its products in the respective countries is given in the treatise on *Petroleum and its Products*, by Sir Boverton Redwood, vol. ii., pp. 216-266, and vol. iii., pp. 1-81, 3rd ed., 1913.

The Pensky-Martens apparatus and that of J. Gray, both of which are employed for determining the flashing point of the heavier mineral oils, are described in the section on "Lubricants," pp. 77 *et seq*.

An important series of experiments with the apparatus used for the determination of the flashing points of illuminating oils has been carried out by J. A. Harker and W. F. Higgins at the National Physical Laboratory, for the International Commission on Petroleum Products.[1]

VI. IGNITION OR "FIRE" TEST.

The temperature at which an oil takes fire on the approach of a flame and continues burning is known as the Ignition or "Fire Test." It may be determined in Abel's apparatus by using it as an open tester. A small flame is brought near to the surface of the oil for a second or two after each rise of $1°$ of temperature, or the lid of the container may be removed after a flashing point determination and the heating continued with periodical applications of the ignition flame.

When the flashing point of an oil is well above the prescribed minimum, the fire test is of little interest and is only determined in special cases.

VII. FRACTIONAL DISTILLATION.

Valuable information as to the composition and true quality of kerosene is afforded by a fractionation test. No fixed standards have been generally accepted, but it is usual to collect and note the distillates below $150°$, from $150°$-$200°$, from $200°$-$250°$, and from $250°$-$300°$; the residue above $300°$ is estimated by difference. The measurements are usually made by volume, from which the actual weights can be ascertained, if required, from the volumes and specific gravities.

The apparatus used for the examination of crude petroleum can be employed for the fractionation (*cf.* p. 6). Other forms of apparatus have been described by J. Biel[2] and by W. Thörner.[3]

VIII. DEGREE OF PURIFICATION.

1. **Sulphur Compounds.**—The presence of sulphur compounds in kerosene gives rise to a disagreeable smell in the products of combustion and vitiates the atmosphere.

They may be estimated by burning a known weight of the oil in a suitable lamp and passing the products of combustion through a cylinder moistened with ammonia, as in the Gas Referees' Test for sulphur in illuminating gas; the sulphur dioxide formed is then oxidised and finally weighed as barium sulphate. This test is fully described in the section on "Illuminating Gas and Ammonia," Vol. II., Part II., pp. 669 *et seq.* As the result of an extended investigation Boverton

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[1] *Petroleum World*, 1911, pp. 303, 351, 397.   [2] *Dingl. polyt. J.*, 1884, **252**, 119.
[3] *Chem. Zeit.*, 1886, **10**, 528, 553, 573, 582, and 601 ; *J. Soc. Chem. Ind.*, 1886, **5**, 371.

Table 12.

Correction of apparent flashing points to the flashing point at normal barometric pressure of 760 mm.

BAROMETRIC PRESSURE IN MILLIMETRES.

FLASHING POINTS IN DEGREES CENTIGRADE.

650	655	660	665	670	675	680	685	690	695	700	705	710	715	720	725	730	735	740	745	750	755	760	765	770	775	780	785
15·5	15·6	15·7	15·8	15·9	16·1	16·2	16·4	16·6	16·7	16·9	17·1	17·3	17·4	17·6	17·8	18·0	18·1	18·3	18·5	18·7	18·8	19·0	19·2	19·4	19·5	19·7	19·9
16·0	16·1	16·2	16·3	16·4	16·6	16·7	16·9	17·1	17·2	17·4	17·6	17·8	17·9	18·1	18·3	18·5	18·6	18·8	19·0	19·2	19·3	19·5	19·7	19·9	20·0	20·2	20·4
16·5	16·6	16·7	16·8	16·9	17·1	17·2	17·4	17·6	17·7	17·9	18·1	18·3	18·4	18·6	18·8	19·0	19·1	19·3	19·5	19·7	19·8	20·0	20·2	20·4	20·5	20·7	20·9
17·0	17·1	17·2	17·3	17·4	17·6	17·7	17·9	18·1	18·2	18·4	18·6	18·8	18·9	19·1	19·3	19·5	19·6	19·8	20·0	20·2	20·3	20·5	20·7	20·9	21·0	21·2	21·4
17·5	17·6	17·7	17·8	17·9	18·1	18·2	18·4	18·6	18·7	18·9	19·1	19·3	19·4	19·6	19·8	20·0	20·1	20·3	20·5	20·7	20·8	21·0	21 2	21·4	21·5	21·7	21·9
18·0	18·1	18·2	18·3	18·4	18·6	18·7	18·9	19·1	19·2	19·4	19·6	19·8	19·9	20·1	20·3	20·5	20·6	20·8	21·0	21·2	21·3	21·5	21·7	21·9	22·0	22·2	22·4
18·5	18·6	18·7	18·8	18·9	19·1	19·2	19·4	19·6	19·7	19·9	20·1	20·3	20·4	20·6	20·8	21·0	21·1	21·3	21·5	21·7	21·8	22·0	22·2	22·4	22·5	22·7	22·9
19·0	19·1	19·2	19·3	19·4	19·6	19·7	19·9	20·1	20·2	20·4	20·6	20·8	20·9	21·1	21·3	21·5	21·6	21·8	22·0	22·2	22·3	22·5	22·7	22·9	23·0	23·2	23·4
19·5	19·6	19·7	19·8	19·9	20·1	20·2	20·4	20·6	20·7	20·9	21·1	21·3	21·4	21·6	21·8	22·0	22·1	22·3	22·5	22·7	22·8	23·0	23·2	23·4	23·5	23·7	23·9
20·0	20·1	20·2	20·3	20·4	20·6	20·7	20·9	21·1	21·2	21·4	21·6	21·8	21·9	22·1	22·3	22·5	22·6	22·8	23·0	23·2	23·3	23·5	23·7	23·9	24·0	24·2	24·4
20·5	20·6	20·7	20·8	20·9	21·1	21·2	21·4	21·6	21·7	21·9	22·1	22·3	22·4	22·6	22·8	23·0	23·1	23·3	23·5	23·7	23·8	24·0	24·2	24·4	24·5	24·7	24·9
21·0	21·1	21·2	21·3	21·4	21·6	21·7	21·9	22·1	22·2	22·4	22·6	22·8	22·9	23·1	23·3	23·5	23·6	23·8	24·0	24·2	24·3	24·5	24·7	24·9	25·0	25·2	25·4
21·5	21·6	21·7	21·8	21·9	22·1	22·2	22·4	22·6	22·7	22·9	23·1	23·3	23·4	23·6	23·8	24·0	24·1	24·3	24·5	24·7	24·8	25·0	25·2	25·4	25·5	25·7	25·9

Redwood[1] arrived at the conclusion that the only satisfactory method for the determination of sulphur compounds applicable to all descriptions of petroleum is that of combustion in oxygen in the Mahler bomb and subsequent estimation as barium sulphate; he recommends that 2 g. of the sample should be burnt, and that the oxygen should be at a pressure of 30 atmos. The results obtained are concordant to the second place of decimals. A description of the Mahler bomb with details of working is given in Vol. I., Part I., in the section on "Fuel," p. 256.

The following method for the determination of the total sulphur in kerosene, by means of the Parr calorimeter, has been proposed by J. M. Sanders:[2]—2-3 g. of the sample are weighed into a 100 c.c. porcelain dish, 0·01 g. of potassium bromide is dusted over the surface, and 4 c.c. of pure fuming nitric acid are added. After the energetic reaction has ceased, the dish is heated on the water-bath until the liquid becomes dark brown and somewhat viscous. It is then well mixed with 0·5 g. of pure light magnesia, and whilst continuing the stirring, is heated over a small flame until the mass shows a tendency to solidify on cooling. The granular mass thus obtained is brushed into a Parr calorimetric bomb, any trace of oily matter left in the dish being removed by warming with a little more magnesia. The standard quantity (1 measure full) of sodium peroxide is also introduced into the calorimeter vessel, and after mixing, the combustion is effected in the usual way. A few seconds after firing, the vessel should be removed from the water in the calorimeter, and its temperature allowed to rise, but not high enough to injure the rubber washer. After about 45 seconds, the bomb is cooled, opened, and the fused mass transferred to 25 c.c. of water in a 200 c.c. nickel beaker, to which the washings are also added. The solution is made slightly acid with hydrochloric acid, filtered through cotton wool if necessary, boiled to expel chlorine, neutralised with ammonia, acidified with hydrochloric acid, and the sulphur precipitated as barium sulphate in the boiling solution. The method is rapid and the results agree with those obtained by the use of the Mahler calorimetric bomb. The construction and use of Parr's calorimeter is described in the section on "Fuel," Vol. I., pp. 256-260.

Good burning oil should not contain more than 0·02 per cent. of sulphur. Commercial oils, even those made from crude Ohio petroleum, usually fulfil this condition. E. Heusler and M. Dennstedt[3] have drawn attention to the presence of alkyl sulphuric acids in kerosene (due to purification by means of sulphuric acid), which, in their opinion, form sulphuric acid on combustion, and increase the tendency of the burning oil to carbonise the lamp-wick.

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[1] *Petroleum and its Products*, vol. ii., p. 319.   [2] *J. Chem. Soc.*, 1912, **101**, 358.
[3] *Z. angew. Chem.*, 1904, **17**, 264; *J. Soc. Chem. Ind.*, 1904, **23**, 317.

2. The Acid Test.—Properly refined petroleum shaken up with sulphuric acid of sp. gr. 1·73 should produce no more than a very slight yellow coloration in the acid.

The official Russian test (Baku section of the Imperial Russian Technical Society) is as follows:[1]—100 vols. of oil are shaken for two minutes at a temperature not exceeding 32° with 40 vols. of the above acid in a stoppered cylinder. The liquid is transferred to a separating funnel and the clear acid drawn off into a glass tube, in which its colour is compared with that of an equal column of a standard solution of Bismarck brown. To prepare the latter, 0·5 g. of Bismarck brown is dissolved in a litre of water; a series of ten standards is then made up by mixing 1, 2, 3, etc., parts of this solution with 99, 98, 97, etc., parts respectively of water, so that the darkest standard (No. 10) contains 0·005 per cent. of the dye, and the lightest (No. 1) 0·0005 per cent. The degree of purification is then expressed by the standard number to which the sample corresponds. Aqueous solutions of Bismarck brown keep fairly well in stoppered bottles.

It has been found in practice that the lamp oil fraction refined on the large scale with 0·5 per cent. of sulphuric acid of sp. gr. 1·84 attains as a rule the colour of standard No. 2. With 0·75 per cent. of acid a slightly higher degree of purity is obtained, but no further advantage is gained by increasing the proportion of acid. The majority of commercial oils fall within the range of numbers 1-8. Hence, standard No. 8 is considered the limit beyond which an oil must be regarded as insufficiently purified.

3. Determination of Acidity.—100 c.c. of oil dissolved in neutralised alcohol-ether should give with one drop of decinormal alcoholic sodium hydroxide a pink colour, phenolphthalein being used as indicator.

4. Salts of Naphthenic and Sulphonic Acids.—The presence of these salts, which impair the burning properties of lamp oil, are detected by extracting the oil with dilute alkali hydroxide in the following manner :—300 c.c. of the oil are placed in a stoppered 500 c.c. flask with 18 c.c. of sodium hydroxide solution of sp. gr. 1·014, heated to about 70° on the water-bath, and thoroughly shaken for one minute. The aqueous layer is separated off, cleared by filtration if necessary, and divided into two halves. To the first half concentrated hydrochloric acid is added, drop by drop, until the liquid is just acid to litmus or methyl orange. To the second half exactly the same amount of acid is added, and the solution then held immediately over small print. If the print can be read without difficulty, the sample may be considered free from organic salts ; if not, the ash of the oil should be determined. A turbidity does not, however, necessarily prove that naphthenic or

[1] *J. Soc. Chem. Ind.,* 1896, 15, 678.

sulphonic salts are present, since under the influence of light and air petroleum may become sufficiently acid to give a positive indication in this test.

5. **Inorganic Residue (Ash).**—A litre or half a litre of oil is gradually introduced into a retort and distilled off until about 10 c.c. are left behind. The residue is washed with petroleum spirit into a tared platinum dish, evaporated or burnt off, and finally incinerated at a low red heat. Good lamp oil should not contain more than 2 mg. of ash per litre.

6. **The " Breaking " of Petroleum.**—This phenomenon is due to the separation of sodium sulphate or sulphonates from an oil which has been standing for a long time.

IX. UNSATURATED HYDROCARBONS.

Many petroleums, especially those from Galicia and Roumania, contain unsaturated hydrocarbons of the olefinic and benzene series, together with cyclic compounds consisting of partly reduced aromatic hydrocarbons.

According to G. Krämer and W. Böttcher and recent experiments of M. Weger,[1] the quantity of unsaturated hydrocarbons as determined by their solubility in concentrated sulphuric acid (p. 21) forms an important indication of the quality of a burning oil.

A characteristic of these hydrocarbons is that they cause the oil to burn with a reddish flame. Thus Borneo oil burns badly in ordinary lamps, but after the removal of the aromatic hydrocarbons its illuminating power equals that of the best American oils.

X. BURNING QUALITY.

As a practical test of the value of an oil for illuminating purposes, the determination of its burning quality under conditions as near as possible to those of ordinary use is of considerable value.

The following method of carrying out this test is recommended by Boverton Redwood.[2] The oil is burnt in the lamp at a constant temperature of preferably 60° F., the wick being raised to yield the largest flame obtainable without smoke. A camera is employed to register variations in the size and shape of the flame during the test. The oil-chambers of the lamps employed should be of uniform dimensions, and the burners must be tested to ascertain that they give similar flames with the same oils. The wicks employed are examined in a special apparatus in which a given length of wick is arranged to draw, by means of capillarity, an oil of known quality from a vessel

[1] *Chem. Ind.*, 1905, 28, 24 ; *J. Soc. Chem. Ind.*, 1905, 24, 126.
[2] *Petroleum and its Products*, vol. ii., p. 212.

at a fixed temperature; the value of the wick is judged from the quantity of oil drawn out in a certain time, and any defective portion is rejected for testing purposes.

No general agreement has been arrived at as to the extent of diminution that should be allowed in a flame classed as of satisfactory burning quality.

XI. ILLUMINATING POWER.

In its physical principles the photometry of illuminating oils does not differ from that of coal gas. A Bunsen photometer fitted with Lummer and Brodhun's prismatic device is the best instrument to use. A full description of the methods of photometry is given in the section on "Illuminating Gas and Ammonia," Vol. II., Part II., pp. 697-716.

The following points are to be noted with regard to the photometry of petroleum : [1]

1. *Construction of the Lamp.*—A great deal depends on the construction of the lamp in which the oil to be tested is burnt. The mode of air-supply, the shape of the chimney and the height of its constriction, and the kind of wick employed, are also important factors. It is therefore desirable to test an oil as far as possible in a lamp resembling those in which it is usually burnt in practice. One and the same kind of lamp must, of course, be used for comparative tests of two or more oils. Wicks should be dried at 105°, and soaked in the oil whilst still warm.

Lamps for testing should be provided with capacious oil-wells, so that the level of the liquid may change as little as possible during burning.

2. *Adjustment of the Flame.*—With some oils, notably the Russian oils, the burning should be started with a comparatively small flame. For the first five minutes the flame is allowed to reach the constriction of the chimney, and no further; it is then gradually raised during the first quarter of an hour to the maximum height, that is, until flickering or smoking ensues on increasing the height of the flame. The position of the constriction should be such that a fully developed flame possesses the maximum of illuminating power. For accurate photometric work the height of the flame should be measured.

3. *Photometric Measurements* are not carried out until the flame has burnt at full height for at least half an hour. In accurate work the measurements are repeated after 4, 5, 6, etc., hours of burning.

When an oil contains an undue proportion of fractions boiling above 270°, its inferior character is only displayed after several hours' burning; a marked diminution of its illuminating power then sets in.

4. *Consumption of Oil* is determined by weighing the oil-reservoir before and after a series of tests. The final results are stated as mean

[1] Eger, *Chem. Rev.*, 1899, p. 81.

photometric intensity, total consumption of oil, and consumption per candle-hour. The height and weight of the charred portion of the wick are noted, as also odour, etc.

5. In special cases the residue remaining after half the oil has been burnt is submitted to fractional distillation, and the result compared with the fractionation of the original oil.

6. *The Standard of Light* in England is the Harcourt 10-candle pentane lamp, in America the International Standard Candle (since April 1909), in Germany the Hefner amyl acetate lamp, and in France the Carcel lamp. A comparison of photometric standards and units is given in the section on "Illuminating Gas and Ammonia," Vol. II., Part II., p. 703.

XII. SOLUBILITY IN ABSOLUTE ALCOHOL.

Lamp oil is soluble in twice its volume of absolute alcohol, and in many cases in less at the ordinary temperature. According to S. Aisinman,[1] all petroleum fractions with a specific gravity up to 0·835 are miscible with absolute alcohol in all proportions.

XIII. DETERMINATION OF THE ORIGIN OF A PETROLEUM.

As it is sometimes of importance to ascertain the origin of a petroleum, various investigations have been made with this object in view.

When a drop of bromine is added to 2-3 c.c. of American petroleum it is decolorised almost instantaneously, whereas all other oils remain coloured for a considerable time. Hence, several determinations have been made both of the iodine and bromine values of petroleum. The following iodine values were found by E. Graefe:[2]—

	Iodine value.
Solar oil (probably a Saxo-Thuringian oil) . .	80
Russian petroleum	0 to 16
American petroleum	5·5 „ 16·5
Galician petroleum	0·1
Wietze petroleum	0·7

The following bromine values were determined by F. Utz:[3]—

Source of petroleum.	Bromine value.
Russia	0·72 to 0·8
Roumania	0·56 „ 0·8
Austria	0·88
Galicia	1·44
Pennsylvania	2·0
Petroleum arc-light	2·56

[1] *Dingl. polyt. J.*, 1895, **297**, 44 ; *J. Soc. Chem. Ind.*, 1895, **14**, 812.
[2] *Z. angew. Chem.*, 1905, **18**, 1580.
[3] *Petroleum*, 1906, **2**, 43 ; *J. Soc. Chem. Ind.*, 1906, **25**, 1140.

No definite conclusions can, however, be derived from these figures,[1] nor can any reliability be placed on the colour test proposed by C. Heragem.[2]

D.—GAS OILS FROM CRUDE PETROLEUM.

The oils used for the production cf gas are obtained from crude petroleum, lignite tar, and shale oil tar. These oils are mobile liquids, of a pale to dark yellow colour; as regards boiling point, they are intermediate between burning oil and lubricating oil, i.e. they boil between 300° to 400°. They are generally soluble for the most part in two volumes of alcohol at the ordinary temperature. Occasionally gas oils of lower boiling point are met with, and these are, like petroleum, easily soluble in two volumes of alcohol.

As a rule, 1 kg. of gas oil yields about 500-600 l. of gas, 300-400 g. of tar, and 40-60 g. of coke.

Further details in regard to gas oils, together with a full account of the methods employed for their examination and valuation, are given in the section on "Illuminating Gas and Ammonia," Vol. II., Part II., pp. 626-629.

E.—TRANSFORMER OILS.[3]

The chief requirements for oils used for high-tension electrical transformers are freedom from moisture and mineral acids. Further, they should exhibit little or no volatility at 100°; hence, many electrical works specify a flashing point of not below 160° (open test). When kept for several hours at 100° the oil should show no signs of decomposition; it should remain quite liquid at the lowest winter temperature, say—15°, to which it may be subjected in practice.

Formerly heavy rosin oil was used for transformers on account of its low price, but to-day the higher petroleum fractions, more or less identical with lubricating oils, are preferred. Thus, a good transformer oil is specified as follows:—Petroleum distillate of viscosity (Engler) 9.8; sp. gr. 0.8825; flashing point 185°; loss after five hours' exposure to 100° in Archbutt apparatus (see p. 74), 0.06 per cent., and after two hours at 170°, 1 per cent. Some electrical works stipulate a viscosity not exceeding 8 (Engler) at 20°.

Rosin oils are considerably more volatile at 100° and 170° than heavy or even light petroleum lubricants. After five hours at 100° rosin oils lose 0.4 to 0.8 per cent. After two hours at 170° thick rosin oils lose

[1] Cf. F. Schwarz, Mitt. Kgl. Materialprüfungsamt. Gross-Lichterfelde, 1909, 27, 25; J. Soc. Chem. Ind., 1909, 28, 467.

[2] Chem. Zeit., 1909, 33, 20; J. Soc. Chem. Ind., 1909, 28, 83.

[3] Cf. A. Duckham, Electrician, 1911, 67, 212; F. Breth, Petroleum, 1911, 7, 290; A. Beringer, Mitt. K.K. Tech. Gewerb. Museum, Vienna, 1911, 21, 211; J. Soc. Chem. Ind., 1912, 31, 114.

5·6 to 7·4 per cent. Light lignite oils show much higher losses at 100°, and are therefore unsuitable for use with transformers.

Those machine oils derived from petroleum which have a flashing point of over 160° (open test) with a volatility of less than 0·1 per cent. in five hours at 100°, provided they satisfy the electrical requirements, are suitable for use in transformers. Rosin oils do not meet these requirements.

Oils serving as high-tension switch insulators must be free from moisture and acid, and must above all be practically non-volatile, so as not to be liable to catch fire from a spark. Cylinder oils are the best adapted to this purpose.

Transformer oils are tested for electrical insulating properties, not by determining the ordinary insulation resistance, but by measuring the E.M.F. requisite to send a spark through a column of oil of definite length. A spark gap is set up within a cylindrical glass vessel of about 200 c.c. capacity and 3 cm. diameter containing the oil, and the E.M.F. is raised until a spark passes. The terminals must be polished spherical knobs, and their distance apart must be kept fixed. Bubbles of water or air and floating fibrous matter affect the results very seriously.

F.—LIQUID FUEL FOR INTERNAL COMBUSTION ENGINES.

Petroleum distillates of all grades—from the light petrol to heavy fuel oils—form the principal liquid fuels employed in internal combustion engines. In addition, coal-tar oils, lignite-tar oils, and even crude tar are used to a small extent in the most modern forms of Diesel engine.

For high speed motors petrol is the usual fuel. With the spray carburettors now employed heavier grades of petrol are serviceable; the average specific gravity is about 0·72. Many modern carburettors are capable of giving a good mixture with air with petrol of higher density, that of sp. gr. 0·76 being employed for motor-bus vehicles and others of similar type. The gross calorific value of petrol is about 11,100 calories per pound; the net value 10,200 calories.

The specific gravity alone is but a rough guide to the character of the petrol. A distillation test should be conducted to ascertain the various fractions over given ranges of temperature. A good petrol of sp. gr. 0·71 will yield nearly 80 per cent. below 120°, and 90 per cent. below 140°.

Benzene (90 per cent. benzol) is an efficient substitute for petrol. In many cases the two liquids are employed, mixed in various proportions. The calorific value of benzol is 9900 calories gross, and 9500 calories net per pound.

In slow speed oil engines ordinary kerosene is employed on a large scale. Owing to its low vapour tension at ordinary temperatures, the kerosene has to be vapourised by heat before admixture with air.

The Diesel engine, with the semi-Diesel type which followed the introduction of the Diesel principle, are not dependent on the formation of an explosive mixture, but on the steady combustion of a fine oil spray through a great portion of the working stroke. The introduction of this type of engine has extended enormously the range of liquid fuels available for power.

Heavy petroleum oils are employed usually, but the very great advantage of being able to use coal-tar and lignite-tar oils cannot be overestimated in countries depending on foreign supplies for all petroleum products. With the latter oils a small quantity of a petroleum oil is injected by an independent pump, to serve as the means of ignition of the coal-tar oil forming the major bulk of the fuel. Since a fine spray has to be produced, it is essential that the tar or tar oil shall contain but little free carbon.

G.—FUEL OILS (MASUT, ASTATKI).[1]

Crude oils, liquid still-residues (Masut), tar residues, cheap lignite tar oils, etc., are largely used, where economic considerations permit, for steam-raising purposes under locomotives, marine engines, and other boilers. The oils must be atomised by some suitable injector, these being operated either by steam, air under pressure, or by forcing the heated oil under pressure through special atomisers.

The examination of fuel oils consists essentially in the determination of the calorific value and the specific gravity. The flashing point is also invariably determined on account of safety in use. In the British Mercantile Marine oil is not permitted for fuel purposes unless the flashing point is above 150° F.

The calorimetric value is determined in a Berthelot, Kröcker, or Mahler bomb (see Vol. I., Part I., p. 254); it can also be calculated from the elementary composition by means of the following formula given by Mendelejeff:—

$$Q = 81C + 300H + 26(O - S).$$

According to the revised Admiralty specification[2] (1912) for oil fuel the flashing point shall not be lower than 175° F. close test, Abel or Pensky-Martens. (In the case of oils of exceptionally low viscosity, such as distillates from shale, the flashing point must not be less than

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[1] Cf. Zaloziecki and Lidow, Naphtha, 1904, Nos. 21, 2e.
[2] Cd. 7010. J. Soc. Chem. Ind., 1913, 32, 859.

200° F.) The proportion of sulphur contained in the oil shall not exceed 3·00 per cent. The oil fuel supplied shall be as free as possible from acid, and in any case the quantity of acid must not exceed 0·05 per cent., calculated as oleic acid when tested by shaking up the oil with distilled water, and determining by titration with decinormal alkali the amount of acid extracted by the water, methyl orange being used as indicator. The quantity of water delivered with the oil shall not exceed 0·5 per cent.

The viscosity of the oil supplied shall not exceed 2000 seconds for an outflow of 50 c.c. at a temperature of 32° F., as determined by Sir Boverton Redwood's standard viscometer (Admiralty type for testing oil fuel). The oil supplied shall be free from earthy, carbonaceous, or fibrous matter, or other impurities which are likely to choke the burners.

H.—DUST-LAYING OILS.

The most suitable dust-laying oils for roads are crude oils, heavy asphalt oils, oily by-products, tars, liquid asphalt, and emulsions of oils and water (Westrumite). Raschig has recently proposed a mixture of tar and clay under the name of "Kiton."

An extensive series of dust-laying oils was investigated by R. Heise,[1] who concluded that the so-called water-soluble oils (see p. 102), which are diluted with water before use, are not to be recommended. Thin pure mineral oils are considered by him to be the most efficient.

Dust-laying oils used for wooden floors and linoleum should be pure mineral oils of high specific viscosity, and should give no separation of sticky substances in the course of a few weeks.

I.—PARAFFIN WAX.

Crude paraffin wax or paraffin scale always contains some of the high-boiling hydrocarbons from which it has crystallised on cooling. The "scale" is subsequently refined to form the paraffin wax of commerce.

Hard paraffin wax for the manufacture of candles should melt at about 50.° Soft paraffin wax, prepared by cold-pressing comparatively light oils, melts at about 30°, and is used for impregnating textiles, etc., and as an addition to hard candle-paraffin.

The examination of hard paraffin wax is described in the section on "Special Methods employed in the Oil and Fat Industries," this Vol., p. 179.

[1] *Arbeiten aus d. Kais. Gesundheitsamt*, 1909, **30**, part i.

Paraffin Scale[1] contains various quantities of impurities or "dirt" (fibres of press-cloths, sand, etc.), water, and hydrocarbons of low melting point termed "oil," which consists chiefly of "soft paraffin."

Determination of "Dirt."—A weighed quantity of the sample is melted, allowed to subside, the clear paraffin wax poured off, the residue mixed with naphtha or petroleum spirit, the whole transferred to a tared, dry filter paper, washed with the solvent used, dried, and weighed.

Determination of Water.—The scale is strongly heated in a copper flask connected with a condenser, and the distillate collected in a narrow graduated measure in which the volume of water that has distilled over is read off. A little light oil distils over with the water. The condenser tube must be washed out with naphtha or petroleum spirit (previously saturated with water), as a little water usually adheres to the sides.

Determination of Oil.—A quantity of the scale, freed from water and dirt by melting and subsidence, is allowed to cool overnight to a temperature of 15°, the solid residue ground to powder, and a portion treated in a press provided with a pressure gauge to express the oil. For this purpose the sample is wrapped in fine linen press-cloth and a sufficient number of layers of filter paper to absorb all the oil.

These methods for the examination of paraffin scale, which have been agreed upon by the Scottish Mineral Oil Association, have been described with full details by J. S. Thomson.[2]
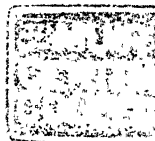
K.—TAR AND PITCH RESIDUES.

(*Petroleum Tar, Asphalt, and Pitch.*)

In the distillation of crude oil a variety of dark-coloured residues are obtained which are used as paving asphalt, lubricants, or as raw materials for the same, and also for a number of other purposes. The more fluid of these residues are sometimes sold directly as cylinder oils; others, which only just melt on the water-bath, may be worked up by "cracking," often with a yield of more than 50 per cent., into dark lubricating oils.

In the examination of these products the testing of their viscosity affords no useful criteria. Their value depends on their *softening point* and *melting point*. The melting point is best determined by G. Kraemer and S. Sarnow's method, which is fully described in the section on "Coal Tar," Vol. II., Part II., p. 837. The results obtained

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[1] *Cf.* Lewkowitsch, *Chemical Technology and Analysis of Oils, Fats, and Waxes*, 4th ed., 1909, vol. iii., p. 211.

[2] *J. Soc. Chem. Ind.*, 1891, **10**, 342.

by this method are consistent in themselves, but, of course, differ for a given substance from the melting point as taken by the capillary tube method. This is illustrated by the following data:—

Table 13.

Material.	Melting point.	
	Kraemer and Sarnow's method.	Capillary tube method.
Ceresin	52°	47° to 53°
Beeswax	55°·5	61°·5 ,, 63°·5
Paraffin wax	46°	45° ,, 48°
Rosin	67° to 67°·5	Indefinite
Asphalt (refined) . . .	51°·5 to 52°	,,
Asphalt (brittle) . . .	82°	,,
Petroleum pitch (Alsatian) .	105°	,,

For the determination of the *specific gravity*, if it be desired only to ascertain whether this is greater or less than 1·0, a fairly large quantity of the sample is melted and a drop or two allowed to fall into a beaker of water at 15°; air-bubbles, if present, must be removed with a feather. For accurate determinations a pyknometer is used.

For the estimation of the content of *Paraffin Wax* the products must first be refined. This is carried out in the same manner as in the examination of ozokerite (p. 55). The paraffin wax is then determined by the method described on p. 179.

The recognition of the presence of *Fat Pitches*, such as are obtained in the candle, wool-fat, etc. industries, is rendered easy by their containing, as a rule, besides hydrocarbons, notable proportions of fatty acids and esters, which are, of course, absent from petroleum. Very hard fat pitches, however, obtained by pushing the distillation to the utmost limit, only contain small proportions of fatty acids and esters. The acid value and the saponification value of these compounds are determined by the methods described in the section on "Oils, Fats, and Waxes," this Vol., pp. 122 and 114.

The subjoined Table gives an indication of the values obtained with "Stearine Pitch," and "Petroleum Pitch," respectively:—

Table 14.

	Stearine pitch.	Petroleum pitch.		Stearine pitch.	Petroleum pitch.
Acids values	0·2	0·1	Saponification values	2·2	1·3
	1·0	0·3		2·4	1·8
	2·4	0·3		4·3	1·7
	2·9	1·2		8·3	2·6
	4·0	...		...	1·1

When soft fatty pitches are destructively distilled considerable quantities of fatty acids are found in the distillate, especially in the first runnings. In the case of hard pitches only the first drops that distil over contain notable amounts of acids; the yield of acids can, however, be considerably increased by distilling with the aid of superheated steam at 300°. The distillate from lignite pitches, on the contrary, contains only minute proportions of acids.

The detection of *Wood-tar Pitch* is facilitated by the characteristic smell of creosote, and by its almost complete solubility in absolute alcohol and in glacial acetic acid, in which petroleum pitch and fat pitches are, for the most part, insoluble. According to E. Donath and B. Margosches,[1] wood-tar pitch differs from all other pitches by its sparing solubility in carbon tetrachloride.

Coal-tar Pitch may be detected by the presence of a considerable amount of free carbon. The best method, however, is to distil the sample destructively and to estimate the anthracene in the distillate by Luck's method, as described in the section on " Coal Tar," Vol. II., Part II., p. 805.

The detection of *Petroleum Pitch in Natural Asphalt* is frequently required. The following method proposed by J. Marcusson and Eickmann [2] can be employed for this estimation :—

30 g. of the sample are dissolved in 45 c.c. of benzene in a small flask under a reflux condenser, and the solution poured into 600 c.c. of petroleum spirit boiling below 80°; the flask is rinsed out with 50 c.c. of petroleum spirit. After standing for some time the solution is sucked off from the asphaltic precipitate, and the filtrate shaken three times successively with 45 c.c. of concentrated sulphuric acid in a separating funnel to remove all asphaltic substances. It is then further shaken with a $N/1$ solution of alkali in 50 per cent. aqueous alcohol and then several times with water, and finally evaporated, dried for ten minutes at 105°, and weighed.

The following data may furnish some guidance in the interpretation of the results so obtained : natural asphalt gave 1·4-31 per cent. of oily matter, yellow-brown to brown in colour, and distinctly liquid at 20°; paraffin wax appeared to be absent, since on cooling the alcohol-ether solution to −20°, only tarry, transparent substances separated out. Petroleum pitch, on the other hand, gave 26-58 per cent. of oily matter of a green to greenish-black colour, which was not liquid at 20° but pasty (sometimes almost liquid and sometimes very viscous), with solid particles; the content of paraffin wax amounted to 3·3-16·6 per cent.

If the quantity of petroleum pitch present is large, it is recommended

[1] *Chem. Ind.*, 1904, **27**, 220 ; *J. Soc. Chem. Ind.*, 1904, **23**, 541.
[2] *Chem. Zeit.*, 1908, **32**, 965.

to distil the pitch destructively, and if small, to distil the oily substances dissolved by petroleum spirit, and to determine the paraffin wax in the distillate.

The detection of petroleum asphalt in natural asphalt may also be based on the comparatively high percentage of sulphur usually found in the latter, which varies from 2-10 per cent.

The above method will be found useful in the examination of *Asphalt Substitutes*, consisting of mixtures of powdered limestone and petroleum pitch. For this purpose it is necessary to first extract the bitumen, which is effected as follows:—

From 2-5 g. of the finely powdered air-dry material are boiled in a conical flask under a reflux condenser with 100-200 c.c. of benzene. The flask is allowed to stand overnight in a slanting position, and the main portion of the clean supernatant liquid is poured off into a second conical flask which is also kept in a slanting position. The solid residue is shaken up with a fresh quantity of benzene, which is allowed to settle as before, and decanted, on the same day, into the second flask. This is allowed to settle overnight, and the clear benzene solution is then finally run off and distilled. The residue is dried at 105° in a tared dish, and weighed. A further quantity of bitumen is extracted from the solid residue by decomposing it with hydrochloric acid and shaking up with benzene. From the total soluble bitumen thus obtained the mineral ash, as determined by incineration, is subtracted. The nature of the soluble bitumen is then examined.

An alternative method for the extraction of the bitumen has been proposed by A. Prettner.[1]

L.—BY-PRODUCTS OF THE PETROLEUM INDUSTRY.

BY-PRODUCTS OF THE REFINING OPERATIONS.

1. Acid Tar.—The acid tar which separates from the concentrated sulphuric acid, used in refining, by dilution with water consists chiefly of resinous substances of unknown composition. It also occludes free sulphuric acid and sulphonic acids. Their determination, which is, however, very rarely required, may be carried out by the methods described under "Turkey Red Oils," in the section on "Special Methods employed in the Oil and Fat Industries," this Vol., pp. 170 *et seq.*

2. Pitch.—This is examined for the melting point and ash, as described in the section on "Coal Tar," Vol. II., Part II., pp. 836 *et seq.*

3. Waste Acid.—This consists of the dilute acid separated from the acid tar, and is valued by the determination of the proportion of actual acid contained.

[1] *Chem. Zeit.*, 1909, 33, 917, 926; *J. Soc. Chem. Ind.*, 1909, 28, 983.

M.—PRODUCTS OF THE SHALE AND LIGNITE INDUSTRIES.

By the destructive distillation of shale and of lignite, tars are obtained which yield crude oils on distillation. These are treated similarly to crude petroleum, and are worked up into naphtha, burning oil, gas oil, and paraffin wax.

EXPERIMENTAL DISTILLATION TEST.

The yield of oil which a bituminous shale or lignite will give is determined by an experimental distillation test.

Scotch oil-shales show considerable differences in the yield of oil. The richer shales yield about 30 gallons of oil per ton of shale, and in some cases as much as 40 gallons, and average about 73 per cent. of mineral matter; Broxburn shale yields 12 per cent. of crude oil, 8 per cent. of water, 9 per cent. of coke, 4 per cent. of gas, and 67 per cent. of mineral residue. A high-grade lignite yields approximately 10 per cent. of tar, 52 per cent. of water, 32 per cent. of coke, and 6 per cent. of gas, including loss. The bituminous shale of Messel (near Darmstadt) yields 6-10 per cent. of tar, 40-45 per cent. of water, and 40-50 per cent. of residue.

A laboratory distillation, although of limited value in estimating the yield obtainable on a large scale, is frequently serviceable. The following method of carrying out the test is recommended :—

A tared retort of refractory glass, holding 150-200 c.c., is connected with a water-cooled receiver fitted with an exit tube, as shown in Fig. 14. From 20-50 g. of the pounded sample are heated, at first with a small and finally with a full flame, as long as any vapours condense. The gases issuing from the receiver, are tested with a flame from time to time ; if the distillation is properly conducted (over four to six hours) they should either not be

FIG. 14.

inflammable, or only burn weakly and fitfully. The distillate, consisting of turbid water and tar, is weighed. The tar which has condensed in the neck of the retort is melted and run down into the receiver; the latter is then placed in hot water, and some hot water poured into it, so that all the tar may collect on the surface. After cooling, the solidified tar is broken up, after the water has drained off. The lumps are dried preliminarily with rolls of filter-paper, then air-dried, and weighed. It is safer to extract the tar by means of benzene, and then to evaporate and weigh the residue. To translate
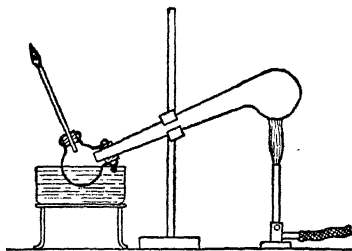
laboratory yields into working yields they must be diminished by a large factor, say by 30-40 per cent., according to the conditions of manufacture. (Lignite tar as produced in works is less acid and specifically lighter than the laboratory product.)

As an alternative to this method, a metal retort and a considerably greater quantity of the sample may be used for the initial distillation.

I. Shale Oil.[1]

The manufacture of paraffin and paraffin oil by the destructive distillation of shale was initiated by James Young in 1851. A highly bituminous mineral known as Boghead coal or Torbanehill mineral was first used, from which a yield of 120 to 130 gallons of crude oil per ton was obtained; the supply of this mineral was, however, exhausted within a few years, and the shales now employed in Scotland, which is the chief centre of the industry, are those found between the Coal-measures and the Old Red Sandstone.

This oil-shale, which is dark grey or black in colour and has a specific gravity of about 1·75, is distilled at a comparatively low tempera-ture. Horizontal retorts were at first employed for the distillation, but vertical retorts and continuous methods of distillation in presence of superheated steam have since been introduced by Young, Henderson, and Beilby, whereby increased efficiency and control of the conditions of working have been effected.

Crude shale oil has a specific gravity of 0·860-0·900, and solidifies at the ordinary temperature; it consists of 70-80 per cent. of paraffins and olefines, small quantities of benzene hydrocarbons and naphthenes, a small proportion of phenol and cresols, and a larger proportion of basic constituents (pyridine, etc.). The refining process comprises fractional distillation, together with treatment with acid and alkali; the solid paraffin is separated from the portion of the oil, the specific gravity of which is above 0·840, by cooling and crystallisation. The commercial products thus obtained vary with the nature of the mineral and the process of distillation adopted; they may be classified under the following headings :—

						Sp. gr.
Gasoline	.	.	.	.	.	0·600 to 0·690
Naphtha or shale spirit	.	.	.	.	.	0·700 „ 0·760
Burning or paraffin oil	.	.	.	.	.	0·760 „ 0·840
Medium or light mineral oil	.	.	.	.	.	0·840 „ 0·870
Lubricating oil	.	.	.	.	.	0·865 „ 0·910
						M.P.
Paraffin wax or "scale"	.	.	.	.	.	43° to 60°

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[1] *Cf.* B. Redwood, *Petroleum and its Products*, 3rd ed., 1913, vol. ii., pp. 83 *et seq.*; I. I. Redwood, *Mineral Oils and their By-Products*; W. Scheithauer, *Shale Oils and Tars and their Products*, English translation by C. Salter; also "The Oil-Shales of the Lothians," *Memoirs of the Geological Survey, Scotland*, 1912.

Gasoline and naphtha contain from 60-70 per cent. of olefines and other hydrocarbons acted upon by fuming nitric acid, burning oil from 30-80 per cent.; lubricating oil consists almost entirely of olefines.

B. Redwood[1] gives the following examples of the average yield of commercial products obtained at two of the principal Scottish refineries in 1895; the grouping of the fractions is somewhat different in the two cases :—.

	I.	II.
Gasoline / Naphtha	6·09	3·0
Burning oil	31·84	39·0
Intermediate and heavy oils	23·97	...
Lubricating oils	...	18·0
Paraffin scale	13·53	...
Paraffin (refined or semi-refined)	...	10·0
Loss	24·57	30·0
	100·00	100·00

The distillation of the bituminous shales of New Brunswick, Canada, and of the United States has been investigated by C. Baskerville.[2]

The Examination of Shale Oil and of Shale Oil Products.

The methods of examination described in connection with petroleum are applicable to the corresponding products from shale oil. These comprise the determination of the specific gravity, the solidifying point, the distillation test, the flashing point, the burning quality, the illuminating value, and the content of " paraffin scale " and paraffin wax.

The *Solidifying Point* of the crude oil is determined by dipping a thermometer into the oil, previously heated to 60°-70°, then withdrawing it and allowing to cool; the temperature at which the drop adhering to the bulb of the thermometer is seen to solidify is taken as the solidifying point. This point is higher the greater the percentage of paraffin present.

The methods for the determination of *Paraffin " Scale "* and of *Paraffin Wax* are described in the section on " Special Methods employed in the Oil and Fat Industries," this Vol., p. 179.

II, Lignite or Brown Coal Tar.[3]

The distillation of brown coal or lignite forms an important industry in Germany; it is not carried on in this country, nor in the United States. The methods of distillation are similar to those employed in the case of shale, and the resulting tar is fractionated and purified for the preparation of commercial products on analogous lines.

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[1] *Petroleum and its Products*, vol. ii., p. 124.
[2] *Eng. and Min. J.*, 1909, 88, 149, 195, and 501 ; *J. Soc. Chem. Ind.*, 1909, 28, 878.
[3] *Cf.* B. Redwood, *Petroleum and its Products*, vol. ii., pp. 124 *et seq.*

At the ordinary temperature lignite tar is a butter-like mass, yellow to brown in colour, and having a smell of creosote and often of sulphuretted hydrogen. The solidifying point ranges from 15°-30°; it begins to boil between 80° and 100°, and the bulk of the distillate comes over, as a rule, between 250° and 350°.

The tar consists mainly of saturated and unsaturated hydrocarbons, of which the former predominate. Owing to the higher proportion of unsaturated hydrocarbons as compared with shale oil the iodine values both of the crude oil and of the paraffin wax obtained from lignite are higher, and amount to 70 and 9 respectively. Other constituents of the tar which are present only to a small extent are phenol, cresols, benzene and its homologues, naphthalene (0·1-0·2 per cent.), chrysene ($C_{18}H_{12}$), and picene ($C_{22}H_{14}$); and in very small quantities, aldehydes, ketones, pyridine bases, quinoline, carbon bisulphide, thiophene and mercaptans.

The Examination of Lignite Tar is conducted similarly to that of shale oil, and the products obtained therefrom are tested in an analogous manner.

For the *Distillation Test of the Crude Tar*, about 200 g. are distilled from a retort. The first runnings, up to the point when a drop crystallises on being cooled with ice, are collected and weighed as light oil, and the subsequent fraction, until reddish resinous matter begins to distil, represents crude paraffin wax; the ensuing picene fraction is collected separately, the residue of coke in the retort weighed, and the gaseous products plus loss taken by difference.

Examination of Gas Oil.—This forms an important fraction of lignite tar. It should be practically free from creosote, which is ascertained by shaking 100 c.c. of the oil with 100 c.c. of sodium hydroxide solution of sp. gr. 1·05 for five minutes and measuring the decrease in volume. The oil should also be free from sulphur. For the *Distillation Test* fractions are collected at intervals of 50°; the greater the proportion of the sample that distils below 300° the greater is its value as a gas oil.

III. Montan Wax.

Montan Wax was first prepared by E. von Bogen[1] from the bitumen extracted from dried Thuringian lignite by means of volatile solvents or from freshly mined lignite by treatment with superheated steam. The resulting product is redistilled repeatedly with superheated steam, and finally distilled in a vacuum. It is used chiefly as a Carnaüba wax substitute in the manufacture of polishes, and as an insulating material in place of ceresin.

The wax forms a hard, white mass, which melts above 70°, and consists of a mixture of fatty acids and a hydrocarbon. The acid

[1] Ger. Pats. 101373; 116453; Eng. Pat., 5999 (1900). *J. Soc. Chem. Ind.*, 1900, **19**, 728; *Z. angew. Chem.*, 1901, **14**, 1110; *J. Soc. Chem. Ind.*, 1901, **20**, 1221.

"Montanic acid" melts at 80°, and has a sp. gr. of 0·915; the hydrocarbon is a saturated compound, melts at 58°-59°, and has a sp. gr. of 0·920. The latter is readily carbonised on heating with concentrated sulphuric acid, a reaction which differentiates it from paraffin wax.

A sample of Montan wax examined by H. Ryan and T. Dillon,[1] which was of a yellowish colour, had a melting point of 76°, an acid value of 73·3, a saponification value of 73·9, and an iodine value (Hübl-Waller) of 16·0. It yielded 47 per cent. of unsaponifiable matter and 53 per cent. of crude montanic acid. The latter had an acid value of 138·3 and consisted in the main of an acid, $C_{28}H_{56}O_2$, with a molecular weight of 432 and a smaller quantity of an acid of lower molecular weight. The unsaponifiable matter had an acid value of 31·3; from its elementary composition it did not appear to be a pure hydrocarbon, but was free from hydroxylic constituents.

Montanin Wax is a similar product to Montan wax, but differs greatly in its physical properties.[1]

N.—OZOKERITE AND CERESIN.

Ozokerite is a naturally occurring bituminous product which is found in several localities in the vicinity of petroleum springs. The best-known product is that from Galicia; it is also found in Roumania, Utah, the Argentine, and the Orange River Colony.[2]

Crude ozokerite varies in colour from yellow to dark brown. The specific gravity varies from 0·91-0·97; the melting point depends upon the proportion of liquid hydrocarbons, and it is accordingly difficult to fix a lower limit, but an upper limit of 100° may be accepted. It is purified from mineral matter, clay, etc., by a liquating process and by boiling out with water, and then consists chiefly of hydrocarbons together with oxygenated and wax-like substances. Fraudulently added impurities comprise asphaltum (mineral pitch) and residues from paraffin-oil distilleries.

In the examination of ozokerite the loss on heating to 150° (which should not exceed 5 per cent.), the melting and solidifying points, and the proportion of mineral matter should be determined. For the estimation of the mineral contents small pieces are cut from the bottom of the blocks and extracted with petroleum spirit.

A reliable valuation of ozokerite can be effected by closely following the method of refining as adopted on the large scale.

The following method for the commercial valuation of ozokerite is recommended by B. Lach:[3]—100 g. of the sample are treated in a tared porcelain basin with 200 g. of fuming sulphuric acid at a

[1] *Proc. Roy. Dublin Soc.*, 1909, **12**, 202; *J. Soc. Chem. Ind.*, 1909, **28**, 878.
[2] *Cf.* J. Berlinerblau, *Das Erdwachs, Ozokerit und Ceresin*, 1897.
[3] *Chem. Zeit.*, 1885, **9**, 905; *J. Soc. Chem. Ind.*, 1885, **4**, 488.

temperature of 170°-180°, with constant stirring, until sulphur dioxide ceases to be evolved, and the basin then allowed to cool, and weighed; the loss in weight represents the sum of the water and hydrocarbons. The residue is then melted and 10 g. of animal charcoal, previously dried at 140°, stirred in. A tenth part of this mixture is weighed off in a paper thimble, extracted in a Soxhlet thimble with petroleum spirit boiling below 80°, and the filter dried at 130° and weighed; this gives the content of ceresin. This result may be checked by evaporating the petroleum spirit solution and drying the residue at 180°; the melting point of the residual ceresin is then determined. The proportion of fuming sulphuric acid used may be varied according as the colour of the refined product is desired to be yellow or white.

According to E. von Boyes,[1] 5 g. of the sample is sufficient for a technical analysis.

Ozokerite is exclusively worked up to-day for the preparation of **Ceresin.** For this purpose it is heated with sulphuric acid, with constant stirring, decolorised with charcoal, and filtered through a filter-press. The cakes thus obtained are then treated with volatile solvents to extract the contained ceresin. The methods of the examination of ceresin are described in the section on "Special Methods employed in the Oil and Fat Industries," this Vol., p. 187.

O.—ICHTHYOL.

By the dry distillation of the bituminous shales containing fossil fish found at Seefeld in the Tyrol, a crude volatile oil is obtained, which when treated with an excess of concentrated sulphuric acid and subsequently neutralised by ammonia yields the product known as "Ichthyol," the ammonium salt of ichthyol sulphuric acid. It has been frequently stated to be a definite compound of the composition $C_{28}H_{36}S_3O_6(NH_4)_2$, but it has been definitely proved by F. W. Passmore,[2] from its behaviour towards solvents, that this is not the case; the sulphur is present both as sulphonate and sulphate, and in addition a portion is derived from the original oil previous to sulphonation ("sulphidic" or non-oxidised sulphur).

According to Passmore, ichthyol contains 10·72 per cent. of total sulphur, of which 5·94 per cent. (reckoned as ammonium sulphate) is present as mineral sulphates. From these figures and other data he calculates the total organic sulphur on the dry organic residue as 18·66 per cent., and that of the "sulphidic" sulphur as 12·51 per cent.

Passmore has also published analyses of a number of preparations of a similar character to ichthyol which have been introduced for medicinal purposes under various trade-names, such as, "Ichthynat,"

[1] *Z. angew. Chem.*, 1898, **17**, 383; *J. Soc. Chem. Ind.*, 1898, **17**, 609.
[2] *Chem. and Drug.*, 1909, **75**, 935.

·" Ichtosan," " Isurol," etc.; these contain from 12·90-16·66 per cent. of organic sulphur, and from 4·07-9·11 per cent. of "sulphidic" sulphur, calculated as above on the dry organic residue.

Ichthyol and the allied preparations are used in medicine chiefly for the external treatment of skin diseases, such as chronic eczema, and as internal antiseptics.

Properties of Ichthyol.—Ichthyol in the form of the ammonium salt is a reddish-brown viscid liquid with a bituminous odour and taste. It is soluble in water, glycerine, oils, fats, and vaseline. Treated with potassium hydroxide, ammonia is liberated, and the mixture after drying and igniting gives off sulphuretted hydrogen when treated with hydrochloric acid. When dried on a water-bath it loses about 45 per cent. of its weight.

P.—PEAT TAR.

In the peat-distilling industry, peat is either distilled right down to coke, which is used in metallurgical operations, or it is only partially carbonised so that the residue may be employed as a household or industrial fuel. The distillates obtained contain respectively 4 or 2 per cent. of tar; 40 or 36 per cent. of products soluble in water, consisting of ammonia, methyl alcohol, and acetic acid; and 21 or 12 per cent. of gaseous products.

To carry out an experimental distillation on the laboratory scale, about 500 g. of the sample are distilled from an iron retort; the works yield of tar may be taken as 70 per cent. of that obtained in the laboratory test. A good peat should not contain more than 6-8 per cent. of ash. The tar contains a considerable proportion (30-40 per cent.) of creosote.

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LUBRICANTS

By Prof. D. HOLDE, Ph.D., Divisional Director of the Royal Testing Laboratory, Gross-Lichterfelde, Berlin, in collaboration with G. MEYERHEIM, Ph.D. English translation revised by the late J. LEWKOWITSCH, M.A., Ph.D.[1]

THE substances used as lubricants may be classified as follows :—

(*a*) **Mineral Lubricants.**—Owing to their cheapness and to certain technical advantages possessed by them, mineral oils enjoy at present by far the widest application. In Western Europe they are imported mainly from America and Russia, to a smaller extent from Galicia and Austria-Hungary ; lubricants are also obtained as one of the products of the Scotch shale-oil industry. Germany produces about one-fifth of its consumption from native material, chiefly from Wietze petroleum.

All mineral lubricants of whatever grade are more or less alike chemically, in that they are composed of petroleum hydrocarbons. There are two chief requirements to which they all must conform. They must not be appreciably volatile, so that loss of volume and risk by fire may be reduced to a minimum, and they must possess a certain viscosity so that they can adhere to the metal surfaces which they are to lubricate, and maintain a film of sufficient thickness between them.

The nature and quality of mineral lubricants vary with the purpose to which they are applied. The principal grades in common use are the following ; the flashing points given are all by the closed test :—

1. *Spindle Oils*, especially adapted to spinning machinery, pale mobile oils of flashing point 160°-200°.

2. *Compressor Oils (Freezing Machinery Oils).*—Thin oils of solidifying point below −20° ; flashing point 140°-180°.

3. *Lubricating Oils for Light Machinery.*—(Oil for shafting, light motors, turbines, and dynamos.) Moderately thick oils of flashing point 170°-220°. Gas-engine oils should flash at 195°-220°.

4. *Lubricating Oils for Heavy Work.*—Thick oils of flashing point 190°-220°.

The above-mentioned varieties are generally refined oils ; they are of a clear yellowish- or reddish-brown colour ; certain high-class oils of groups 1, 2, and 3 are nearly colourless ; compressor oils are sometimes

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artificially coloured to a violet tint. The cheaper kinds of heavy machinery oil are opaque.

5. *Heavy Railway Waggon and Engine Oils.*—"Summer oil," flashing point above 140°, solidifying point below −5°. "Winter Oil," solidifying point below −20°.

6. *Cylinder Oils* represent the highest boiling fractions of petroleum. They are mainly the still residues of the lubricating oil fractions of heavy consistency; they congeal to vaseline-like masses at ordinary temperatures or a few degrees above 0°. Those oils, which have been filtered over fuller's earth, are brownish-red and translucent; undistilled and unfiltered oils are greenish-black and opaque. In reflected light the paler American oils show a greenish-grey, the Russian oils a bluish fluorescence. The flashing points range from 220°-315°, the better qualities flashing not below 260°. Superheated oils flash at from 280°-300°, or even higher.

(*b*) **Fatty Oils and Liquid Waxes.**—The chief kinds employed as lubricants are crude and refined rape (colza), olive, castor, animal oils (lard, tallow, neat's foot, bone, etc.), sperm and arctic sperm oils, and palm oil. Even blubber oils and also wool-grease are occasionally used as lubricants.

(*c*) **Mixtures of Fatty and Mineral Oils** are used frequently. For marine engines a mixture of blown rape oil and a mineral oil sold as "marine oil" is largely employed. Mineral cylinder oils often receive an admixture (2-12 per cent.) of bone fat.

(*d*) **Lubricating Greases** are employed to some extent on account of their easy and, in certain cases, economical application. They consist of solutions of lime-soaps or lime-alkali-soaps in mineral oils, and contain, as a rule, from 2-6 per cent. of water; they usually liquefy at 70° or 80°. Other lubricating greases are mixtures of wool-grease, tallow, alkali-soaps, etc., with mineral oil. Lubricants containing graphite are employed as lubricants for cog-wheels, bicycle chains, and the like. This class of lubricants is likely to be replaced in the near future by the Acheson Graphite Company's compounds ("Oildag," "Aquadag").[1] The lowest class of lubricating greases is represented by the axle and waggon greases; these contain lime-soaps, rosin oil, lignite-tar or coal-tar oils, also magnesium silicates such as talcum. The cheapest products are adulterated with barytes, plaster of Paris, etc.

(*e*) **Water-Soluble Oils** have the property of yielding homogeneous emulsions with water, and are prepared by dissolving ammonia- or alkali-soaps in pale mineral oils (sometimes with the addition of petroleum naphtha). They are chiefly used for lubricating tool-machines, for charging hydraulic presses and conduits, for oiling yarn in the textile industries, and as dust-laying oils.

[1] *Cf.* Archbutt and Deeley, *Lubrication and Lubricants*, 3rd ed., 1912, pp. 150 *et seq.*

(*f*) **Thickened Oils.**—For some purposes mineral oils are thickened by dissolving in them small amounts of unvulcanised rubber or of aluminium sulphate.

(*g*) **Non-Oleaginous Lubricants.**—There are a few exceptional cases in which oily lubricants would be dissolved or chemically attacked, and are therefore inapplicable. In chlorine and oxygen compression plants, for example, strong sulphuric acid and dilute glycerine respectively are the lubricants used. In the sulphur dioxide industry the liquid sulphurous acid itself acts as a lubricant for the pistons and cylinders.

A.—MINERAL OILS.

PHYSICAL TESTS.

I. APPEARANCE.

A practised observer can derive valuable information from the colour, transparency, smell, and consistency of a lubricating oil. The odour of an oil is best observed by rubbing a drop or two in the palm of the hand.

(*a*) **Colour.**—The colour of an oil is conveniently noted in a thickness of 10 cm. In special cases the examination may be carried out either with Lovibond's tintometer,[1] or with Stammer's colorimeter (see the section on " Mineral Oils," p. 23).

Colour varies, according to the degree of purification, from water-white to dark red by transmitted light. Pale oils (not treated with nitronaphthalene or aniline dyes to render them non-fluorescent) invariably show a fluorescence, which is green in the case of American oils and bluish in the case of Russian oils.

Fluorescence is best ascertained by observing a drop of oil upon glazed black paper; fluorescent oils appear blue, whilst treated oils appear simply black. For the detection of deblooming substances such as nitronaphthalene, etc., see p. 94.

Oils containing still residues in notable quantity and not filtered over fuller's earth are opaque and very dark. Machinery oils are almost without exception transparent.

Unfiltered cylinder oils have an opaque greenish- or brownish-black appearance. If filtered or mixed with filtered residues they are dark red and translucent. Solid, readily melting particles separating in thin layers from the oil are, as a rule, paraffin wax, pitch, or ozokerite; the latter material is added as a thickening agent to certain Russian cylinder oils.

A slight turbidity in pale oils is frequently due to suspended water.

[1] Cf. *J. Soc. Chem. Ind.,* 1888, **7**, 424 ; 1890, **9**, 10 ; 1894, **13**, 308.

(*b*) Consistency.—Cylinder oils are liable, owing to changes of temperature and agitation immediately before examination, to present very puzzling indications. It is best to pour such oils into a test tube 15 mm. in diameter and 3 cm. high, warm for ten minutes in the water-bath, and allow to cool for one hour in water at 20°. The consistency is then observed on inclining the test tube.

(*c*) Mechanical Impurities are easily recognised in pale oils. Dark oils must be passed through a sieve of $\frac{1}{3}$ mm. mesh; not less than 250 c.c. should be poured through the sieve.

II. SPECIFIC GRAVITY.

The specific gravity of mineral lubricating oils is of importance only when oils of known definite origin are to be compared, or as a means of identification, although it is usual in commerce to sell the oil with a statement as to the specific gravity.

Determination of the Specific Gravity by Means of the Hydrometer.

(*a*) Standard Hydrometer. — The specific gravity of mineral oils (and liquid fats or waxes) may, if sufficient material is available, be determined by means of a reliable hydrometer.

In Germany officially calibrated hydrometers, standardised for +15° C., water at +48° being the basis, are obtainable ; Tables specially adapted to American petroleum and its products have been prepared by the Normal-Eichungs-Kommission of Germany.[1] The temperature of the experiment is determined by a thermometer attached to the hydrometer spindle.

Hydrometer readings are, whenever possible, taken at the flat level of the liquid, viewed from below; but when the oil is too dark, it is necessary to read at the upper edge of the meniscus and to add 0·0015 or 0·0010, according to the dimensions of the scale, to the specific gravity found. Care must be taken that the hydrometer floats freely in the liquid; the reading should not be taken before fifteen minutes have elapsed after the immersion of the hydrometer.

The specific gravity is corrected to the standard temperature of 15°. For each degree difference between the observed and standard temperature a correction of ±·00068 is made.

Example.

Hydrometer reading at 17°·5 .	0·9910
Meniscus correction . . .	+0·0010
Temperature correction, 2·5 × ·00068 .	+0·0017
Specific gravity at 15 . .	0·9037

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[1] Published by J. Springer, Berlin.

The following Table, worked out by Mendelejeff, gives the temperature corrections for high-boiling Russian petroleum oils:—

Table 15.

Sp. gr. of fraction.	Correction per 1°.
0·860 to 0·865	0·000700
0·865 ,, 0·870	0·000692
0·870 ,, 0·875	0·000685
0·875 ,, 0·880	0·000677
0·880 ,, 0·885	0·000670
0·885 ,, 0·890	0·000660
0·890 ,, 0·895	0·000650
0·895 ,, 0·900	0·000640
0·900 ,, 0·905	0·000630
0·905 ,, 0·910	0·000620
0·910 ,, 0·920	0·000600

(b) **Determination of the Specific Gravity by Pyknometers.**—

FIG. 15.

If great accuracy is required, or if there is not enough oil available to use a hydrometer, a pyknometer, such as the ordinary Sprengel tube or a Mohr's balance, is employed for the determination of the specific gravity.
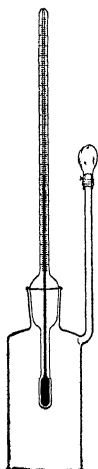
A serviceable form of pyknometer devised by Göckel for highly viscous oils 'is shown in Fig. 15; it has a capacity of 10 c.c. at 15° and is fitted with' a ground-in thermometer. If the calibration is correct, the absolute weight of the sample divided by 10 gives the specific gravity at 15° without further calculation. Correction to standard temperature and water at 4° is made by the aid of the data given above.

If only a few cubic centimetres of the sample are available, a small pyknometer is used.

In order to determine the specific gravity of pitch-like lubricants heavier than water, the pyknometer is employed as follows. A small quantity of the substance, melted if necessary, is poured on the bottom of the vessel and allowed to cool; the pyknometer is then weighed, filled up with water, and again weighed.

(c) **Determination of the Specific Gravity by the Flotation Method.**—The specific gravity of very small quantities of a lubricant

may be determined, provided the substance is insoluble in dilute alcohol, by floating it in dilute alcohol of identical density.

Table 16.

Specific Gravity of various Oils at 15°.

	American.	Russian.
Lamp oil	0·780 to 0·800	0·800 to 0·830
Spindle oil	0·840 ,, 0·907	0·850 ,, 0·900
Machinery oil . . .	0·875 ,, 0·914	0·900 ,, 0·915
Cylinder oil . . .	0·883 ,, 0·895	0·909 ,, 0·932
		(exceptionally up to 0·950)
Heavy rosin oil		0·973 to 0·982
		(exceptionally up to 1·000)
Coal-tar oil		1·090 to 1·100
Lignite-tar oil		0·893 ,, 0·974

Preliminary trials are made by dropping a little of the oil or melted fat into a series of mixtures of alcohol and water of progressive densities, in order to ascertain approximately the upper and lower limits. The liquid nearest to the substance in specific gravity is then adjusted, by adding very dilute, or as the case may be, absolute alcohol, a thermometer being used as a stirring-rod, until the substance just floats in the liquid without either rising or sinking. The specific gravity of the liquid is then determined accurately; it equals the specific gravity of the sample at the temperature of experiment. It is essential that no air-bubbles adhere to the floating globules of oil.

III. EXPANSIBILITY.

Although coefficients of expansion do not find a place among the commonly accepted characteristic constants of oils, they are required for calculating specific gravities to different temperatures, and especially for calculating the expansion-space to be allowed for transport, and in storage vessels.

The expansibility is determined either by taking the specific gravity at successive temperatures (for corrections for temperature, see p. 65) or by a dilatometric method. For the latter purpose an apparatus which allows of the simultaneous examination of eight samples has been devised by Holde (Figs. 16-18). The dilatometers (Fig. 16) have the shape of bulbs of about 30 c.c. capacity, with graduated stems 0·7 mm. in bore, holding about 850 cb.mm. The initial volume of oil at ordinary temperatures is adjusted in a large water-bath arranged like a calorimeter as shown. For higher temperatures the water-bath B is placed in a vapour-bath A (Fig. 17) heated by a Bunsen burner.

The vapourising liquid, which is chosen according to the temperature required, may be ethyl ether (boiling point 35°), ethyl bromide (boiling point 38°), chloroform (boiling point 61°), carbon bisulphide, alcohol, . or any other suitable liquid. Reflux condensation is provided for at e. A number of dilatometers, together with a thermometer graduated to tenths of a degree, are suspended by means of rubber rings in the water-bath. Fig. 18 illustrates the method of charging the. dilatometers with oil by suction with a copper or brass capillary tube; discharging is performed similarly by blowing in air. Air bubbles remaining at the junction of the bulb and stem can usually be removed by judicious use of the suction-capillary. Any oil adhering
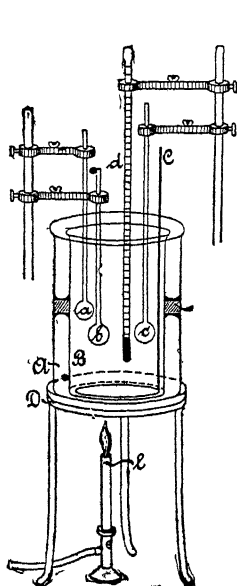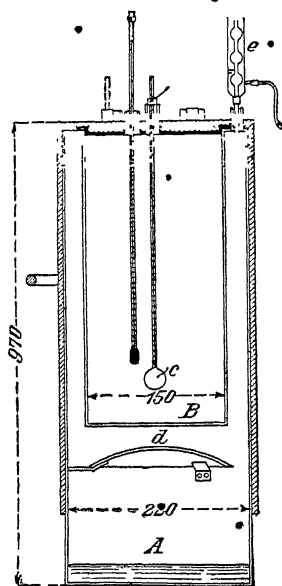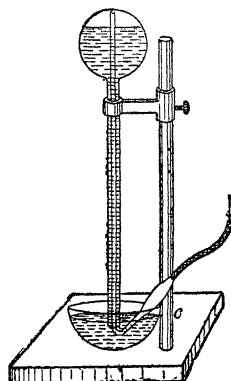
FIG. 16. FIG. 17. FIG. 18.

to the upper part of the stem is wiped away by means of a spiral wire wound with cotton wool.

The stems of the dilatometers are carefully calibrated, once for all, with the aid of mercury. To empty the mercury for the purpose of weighing, a thread of glass, which is weighed with the receiving beaker, is pushed up the stem. The volume of the dilatometer up to the zero mark is determined by weighing it filled with water; in this case the weighings must be reduced to vacuum, which is unnecessary in the case of the mercury thread calibration.

The coefficient of expansion a is calculated by the following formula :—

$$a = \frac{V_1 - V}{(t_1 - t)V} + c$$

·where V is the initial volume at temperature t, V_1, the greater volume at the higher temperature t_1, and c the cubic expansibility of glass, which may be taken as 0·000025, or may be ascertained by determining the apparent expansion of the mercury before the experiment.

For heavy viscous machinery and axle oils of sp. gr. not less than 0·908, the value of α between 20° and 78° is 0·00070-0·00072. Oils of this class from which particles of wax or pitch separate out at and below +20° show a higher value between 12° and 20°, namely, 0·00075-0·00081.

For light spindle and dynamo oils, of sp. gr. less than 0·905 at 15°, the value of α is 0·0072-0·00076 between 20° and 78°.

In the case of oils which are homogeneous liquids, the value of α increases slowly with the rise of temperature.

When an oil contains fusible matter in suspension, α decreases with rising temperature up to the point when all the suspended particles are liquefied, and then increases as in the case of a homogeneous liquid.

In the case of oils of different origin but of equal viscosity, a difference in expansibility corresponds to a difference in chemical composition..

According to Singer,[1] Roumanian petroleum residues have an expansibility of 0·00073-0·00079.

Specific Gravity Correction.—In recalculating the specific gravity from a higher to a lower temperature, or *vice versâ*, the allowance per 1° for liquid mineral lubricants is 0·00063-00072, or 0·00065 as a mean value.

When specific gravities are determined by the pyknometer at temperatures above 30°, allowance must, in addition, be made for the expansion of the pyknometer itself.

In the case of vaseline-like lubricants or of very viscous cylinder oils, for which α ranges from 0·000777-0·000876,[2] a mean correction of 0·00075 per 1° may be taken.

IV. VISCOSITY.

The accurate determination of the internal friction of liquids requires the use of apparatus which is unsuited for technical work. For practical purposes more simple apparatus is employed, by means of which a relative determination of viscosity is effected. The determination is usually made by ascertaining the times occupied by two equal volumes of the liquids under comparison to flow through a narrow aperture under exactly the same conditions. The numbers thus obtained are entirely arbitrary, and are different with the various forms of apparatus, viscometers, employed for the purpose.

The viscosity of oils is, in practice, generally compared with that of

[1] *Chem. Rev.*, 1896, **13**, 298.   [2] *Mitteilungen*, 1895, Ergänzungsheft, v., p. 23.

rape oil. Boverton Redwood[1] found from a number of tests carried out with refined rape oil in his viscometer that the average time occupied by the outflow of 50 c.c. at 60° F. (15°·5 C.) is 535 seconds. Taking this as a standard and its viscosity as = 100, the viscosity of any other oil is found by multiplying the number of seconds occupied by the outflow of 50 c.c. by 100 and dividing by 535. If the specific gravity of the oil differs from that of rape oil, which is 0·915 at 60° F., Redwood introduces a correction by multiplying the above result by the specific gravity of the sample and dividing by 915.

The viscosity of an oil, V, is therefore obtained from the equation :—

$$V = \frac{n \times 100 \times s}{535 \times 915}$$

where n is the time of outflow and s the specific gravity of the oil under examination.

As there is no correlation between the specific gravity and viscosity of an oil, it is more useful to record the numbers as obtained by the direct determination of the viscosity, and to omit the specific gravity correction (Lewkowitsch).

Of the many forms of viscometer that have been designed, those of Redwood, of Saybolt, and of Engler are the most important. Redwood's apparatus is the recognised standard instrument in this country, and has been adopted by the Government, by the principal Railway Companies, and by the Scottish Mineral Oil Association. Saybolt's viscometer is used in the United States, and that of Engler in Germany, and generally on the Continent. In France an instrument known as an " Ixomètre," designed by Barbeys, is employed.

Boverton Redwood's Viscometer.[2]—This instrument, which is shown in Fig. 19 and in section in Fig. 20, consists of a silvered copper oil-cylinder C, about $1\frac{7}{8}$ in. diameter and $3\frac{1}{2}$ in. deep. The bottom of the cylinder is provided with an agate jet D, the cavity of which can be closed by means of the plug E formed of a small silvered brass sphere attached to a wire. A small bracket F terminating in a point is fixed at a short distance from the top of the inside of the oil cup, and serves as a gauge of the height to which the oil must be filled. The thermometer T is immersed in the oil. The oil-cylinder is surrounded by a copper jacket J, provided with a closed side-tube K, which serves for heating the contained liquid to the desired temperature ; a revolving agitator L, worked by the handle H, is provided together with a thermometer T^1 for recording the temperature of the liquid in the jacket. The whole instrument is supported on a tripod stand furnished with levelling screws.

[1] *J. Soc. Chem. Ind.*, 1886, **5**, 126.   [2] *Ibid.*

To carry out a determination, the copper jacket is filled with water for temperatures up to 95°, and for higher temperatures with a suitable mineral oil, up to a height corresponding roughly with the pointer F in the cylinder C. After the liquid in the jacket has become heated to the required temperature, the oil to be tested, previously purified and dried and heated to the same temperature, is poured into C until its level just coincides with the point of the gauge; great care must be
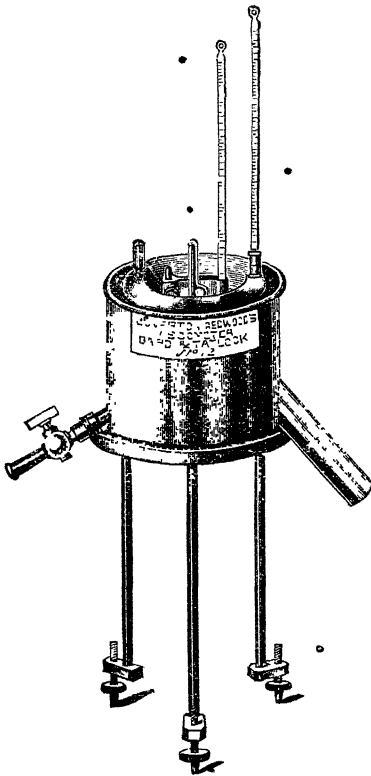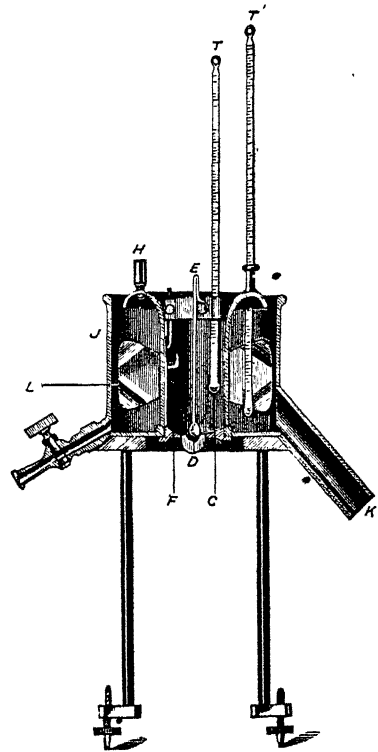
FIG. 19.   FIG. 20.

taken that this level is reached exactly, and that the temperature remains constant during the observation. A narrow-necked flask holding 50 c.c. to a point marked on the neck is then placed below the jet D in a vessel containing a liquid of the same temperature as the oil. The plug E is then raised, and the number of seconds required for 50 c.c. of the oil to flow out is carefully observed by means of a chronometer.

At least two tests should be made at the same temperature; if due care has been taken the two observations should be closely concordant. The viscosity value is then calculated to the standard of rape oil as described above.

Saybolt's Viscometer.—The jet of this viscometer is made of metal, and is enclosed in a tube which extends below the orifice. The oil-vessel is contracted above the jet, and is cut away longitudinally on each side to expose a glass tube with which it is lined, and which can be seen by means of glass windows provided in the water-bath in which the oil-vessel is placed. The upper level of the oil is regulated by means of an overflow gallery, the position of which determines the length of the oil column, and the outflow, which is observed through the windows of the bath, is stopped when the oil reaches a certain point in the inner glass tube of the oil vessel.[1]

C. Engler's Viscometer.—The vessel A (Fig. 21), which serves for the reception of the oil to be tested, is filled with oil up to the tip of
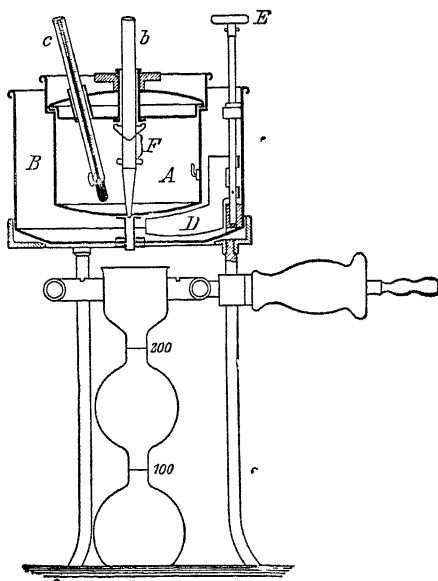
FIG. 21.

a small pointer fixed to the side of the vessel, whilst the efflux tube, which is either made of or lined with platinum, is closed by a wooden rod *b* which passes through the cover *c*. The oil (or water) is caught as it flows out in the measuring flask which is graduated at 200 and 240 c.c. When the measuring vessel has three bulbs as in Fig. 21, and has a graduation mark at 100 as well as at 200, each experiment can be controlled in itself by reading the time of outflow from 100-200 c.c.

In order to heat the oil to the required temperature for the test, the inner vessel is surrounded by a heating jacket B, which is filled either

[1] For further details see Redwood, *Petroleum and its Products*, 3rd ed., 1913, vol. ii., p. 279.

with water or with a high-boiling mineral oil; the heating is effected by a movable ring-burner at least 10 cm. in diameter, and the bath stirred by the stirrer DE, thus avoiding any superheating of the outlet hole; F is a small catch which supports the plunger and prevents it from slipping into the orifice during the experiment.

The expression for the viscosity, generally called "Engler degrees," is the quotient obtained by dividing the time of flow for 200 c.c. of the oil at any specified temperature, by the time of flow of 200 c.c. of distilled water at 20°.

The relative value of viscosity determinations by Redwood's and by Engler's apparatus has been investigated by W. F. Higgins.[1] Calculated from theoretical considerations, the ratio of the readings is approximately constant for times of flow on the Redwood viscometer greater than 100 seconds and is = 1·81 (Engler : Redwood); below this the ratio increases with decrease in the time of flow from 1·82-1·83. Experimental results on three different oils and at temperatures varying between 10° and 45° gave ratios between 1·74 and 1·84.

Viscosity of Mixtures of Oils.

As the viscosity is not an additive property, the viscosity of mixtures cannot be calculated directly from the proportions of the components, but is always lower than the calculated value. According to experiments by H. Sherman, T. Gray, and H. Hammerschlag,[2] if the viscosities are plotted as ordinates and the percentages of the components as abscissæ on squared paper, the relationship between the two is expressed by hyperbolic curves which deviate more strongly from the straight lines joining the extreme points, the more the viscosities differ from one another. Mixtures of different mineral oils give greater deviations from the straight lines than mixtures of mineral with fatty oils.

For the determination of the viscosity of the unsaponifiable portion of a blended oil, the viscometers described above will, as a rule, be found to be too large. In such cases Künkler's viscometer, which requires only 30 c.c. of the sample, will be found useful.[3]

Absolute Viscosity.

The desirability of expressing viscosities in absolute measure, instead of by the arbitrary values at present adopted, has recently received consideration. The absolute viscosities of water and of

[1] *J. Soc. Chem. Ind.*, 1913, **32**, 568.
[2] *J. Ind. Eng. Chem.*, 1909, **1**, 12; *J. Soc. Chem. Ind.*, 1909, **28**, 17.
[3] *Dingl. Polyt J.*, 1893, **290**, 281. *Cf.* also Lewkowitsch, *Chemical Technology and Analysis of Oils, Fats, and Waxes*, vol. iii., p. 52.

glycerol have been determined by L. Archbutt and R. Deeley,[1] and a series of determinations of the absolute viscosities of a number of mineral oils in C.G.S. units has been carried out by W. F. Higgins[2] at the National Physical Laboratory in connection with his work for the International Commission for the unification of tests on petroleum products.

V. BEHAVIOUR OF OILS AT LOW TEMPERATURES.

In order to judge accurately of the consistency of oils when exposed to cold, the following points must be taken into account.

When mineral oils, in passing from the fluid to the semi-solid condition, are disturbed, the network of separated solid matter is ruptured, and the "crystallising" process is greatly affected. In examining oils at low temperatures, therefore, cooling must take place without agitation.

Oils must be cooled during at least one hour to the desired temperature, since the solid particles separate with great reluctance, and temperature equilibrium is attained very slowly. If an oil has been heated before being cooled down, its physical condition is altered to such an extent as to modify the freezing point considerably. In the same way, the effect of alternate cooling and warming to room-temperature is to render the freezing point hopelessly variable. Oils may be exposed to fluctuations of temperature during transportation or storage, and this possibility must be taken into account when they are tested.
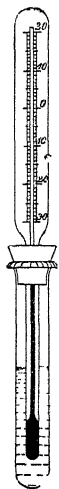
FIG. 22.

Pale heavy mineral oils are sometimes known to set to a jelly whilst remaining perfectly transparent.

The question to be decided is whether, and to what extent, an oil is fluid at a certain temperature, say $-5°$ or $-15°$; or, alternatively, at what temperature solids separate out and the oil becomes semi-solid. Much time is saved by making a preliminary test with the apparatus shown in Fig. 22: the oil is cooled down in a test tube by means of a mixture of ice and salt, and its behaviour on tilting the test tube is observed from time to time. The approximate solidifying point being now known, a series of refrigerating solutions which can be kept at a constant freezing point for an hour or more is prepared, according to the subjoined data. These solutions are partially frozen by means of a mixture of one part of salt and two parts of pounded ice or snow.

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[1] *Lubrication and Lubricants*, pp. 153 *et seq.*
[2] *J. Soc. Chem. Ind.*, 1913, **32**, 568.

Temperature.				Solute.	Parts to 100 of water.
0°	.	.	.	Ice	...
− 3°	.	.	.	KNO$_3$	13
− 4°	.	.	.	{ KNO$_3$ { NaCl	{ 13 { 2
− 5°	.	.	.	{ KNO$_3$ { NaCl	{ 13 { 3·3
− 8°·7	.	.	.	BaCl$_2$	35·8
−10°	.	.	.	KCl	22·5
−14°	.	.	.	NH$_4$Cl	20
−15° to −15°·4	.	.	NH$_4$Cl	25

For most practical purposes it is sufficient to ascertain whether an oil flows or does not flow at the temperature of experiment. The apparatus shown in Fig. 23 may be used with advantage for this
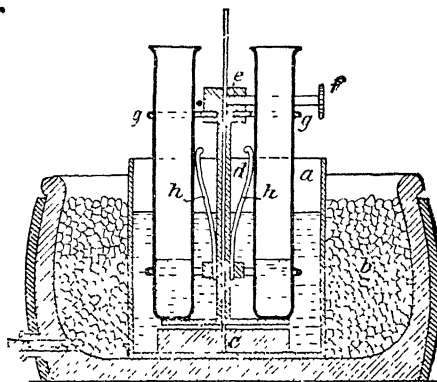
FIG. 23.

purpose.[1] A vessel of enamelled iron a, about 12 cm. wide, holds the standard solution, and is surrounded with a freezing mixture b contained in the earthenware pan c, which is lagged with felt. Test tubes filled up to a mark (3 cm. high) with oil are placed in the holder attached to a. After the samples have been cooled for one hour they are examined as in the preliminary test. A further differentiation as to consistence may be made by placing glass rods in the test tubes for a quarter of an hour, and noting whether the tubes are moved up bodily when the rods are lifted. If the standard refrigerating solution shows any tendency to fall below the proper temperature, the ice which has deposited round the inner sides of the vessel is knocked away and the outer freezing mixture is removed. Temperatures are read by means of a thermometer graduated to tenths of a degree. The freezing mixture may have to be renewed from time to time, but as a rule this is not required, except at the lowest working temperatures.

[1] Cf. Hofmeister, Mitteilungen, 1889, p. 24.

Constant temperatures of $-20°$ to $-21°$ may be maintained by filling both the inner and outer vessels with the freezing mixture of ice and salt. To obtain still lower temperatures a thin metal inner vessel (not enamelled) is used, and both this and the outer vessel are charged with alcohol into which solid carbon dioxide is thrown as required.

Quantitative Comparison of Fluidities. The Freezing Point or Cold Test.

A quantitative statement as to the behaviour at low temperatures is sometimes required for the valuation of dark railway oils, and may be obtained by the aid of the apparatus shown in Figs. 24, 25, and 26.
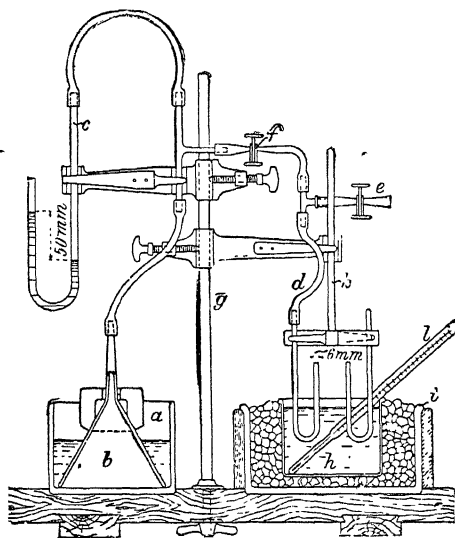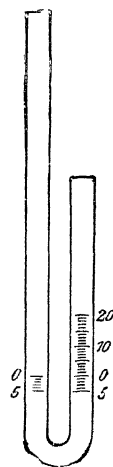
FIG. 24.   FIG. 25.

This determination is not so important in this country as in the United States and on the Continent, where the danger exists of machinery being damaged by the oil becoming solid in the lubricators. Fig. 24 is a diagrammatic representation of the apparatus prescribed for the testing of oils by the Prussian State Railways; Fig. 26 shows the actual form of the apparatus. To carry out the test the oil is thoroughly shaken in the sample bottle, and freed from mechanical impurities by filtration through a sieve of $\frac{1}{3}$ mm. mesh. In order to take the effect of previous heating into account, four tests are made, two with untreated oil, and two with oil which has been heated on the water-bath to $50°$ for ten minutes. In all cases, as also when the simple test described in the preceding paragraph is carried out, it is well to conduct the preliminary heating and cooling in the actual testing vessel, be it a test tube or a U-tube.

The oil is charged by means of small pipettes fitted with a rubber ball into the longer limb of the testing vessel. This latter consists of a U-tube (Fig. 25) of 6 mm. bore, having a millimetre graduation as illustrated. It is important that these tubes should have no constriction at the bend; at no point should the bore exceed or fall short of 6 mm. by more than 0·3 mm. The level of the oil is adjusted to stand at the zero mark, which is 3 cm. above the bottom of the U-tube. The tube is immersed in a vessel h (Fig. 24 in which two tubes are shown) filled with the freezing mixture of the specified temperature, and
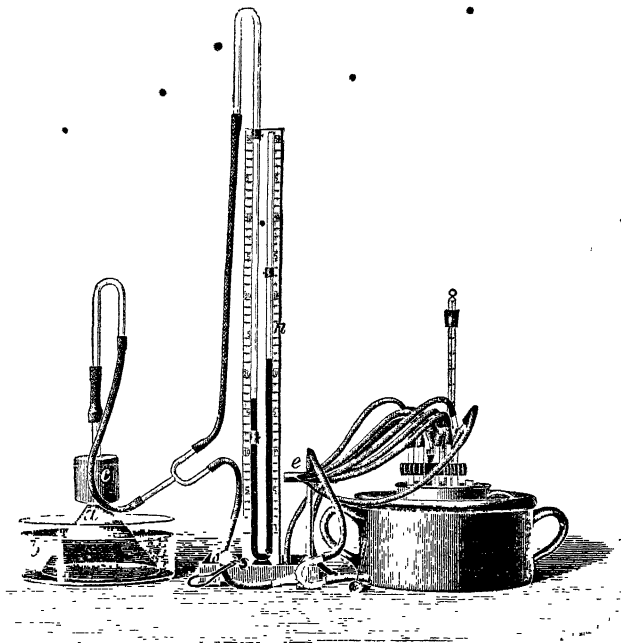
FIG. 26.

surrounded by the vessel i, which is also filled with the freezing mixture; the temperature is controlled by the thermometer l. The U-tube should stand for at least one hour in the freezing mixture without being disturbed, the level of the oil being about 10 mm. below that of the freezing mixture. The tube is then carefully drawn out so far that the level can be observed, when the rubber tube d is slipped over its end whilst the pinch-cock e is open. This pinch-cock is then closed and the pinch-cock f opened, whereby a pressure of 50 mm. is allowed to act on the oil; this pressure is generated by pouring water into the vessel a, in which a weighted funnel b is placed, and controlled exactly by the manometer c. The height to which the sample of oil has risen when compressed is read off on the shorter limb of the U-tube, the oil

adhering to the sides showing the required level even though the body of oil may have sunk a little; this height expresses quantitatively the fluidity of the sample under compression.

The Scottish Mineral Oil Association directs that the setting point of mineral oils be determined in the following manner:[1]—Place the sample in a test tube, having a diameter of $1\frac{1}{4}$ in., to the depth of about 2 inches. Immerse the test tube in a freezing mixture and stir the oil slowly with a thermometer until it has cooled down considerably below the temperature at which solid paraffin wax first appears. Then remove the test tube from the freezing mixture, stir constantly with the thermometer, and observe the temperature at which the last trace of solid paraffin wax disappears. The temperature thus found is the setting point.

VI. VOLATILITY AND INFLAMMABILITY.

Within certain limits, volatility runs parallel with the flashing point, which latter is readily determined either by the "open" or "closed" test. Thus the quality of machinery and cylinder oils may, so far as volatility is concerned, be judged by their flashing points.

Flashing points, however, are not reliable criteria of volatility unless they lie above the minimum admissible limit, i.e., unless lower petroleum fractions are absent. To decide this point it may be necessary to undertake a fractionation of the oil, or to determine the loss in weight on heating in an open vessel. The fixing of minimum flashing points for the various sorts of lubricating oils is a great desideratum. When lower fractions are absent, the distillation test is useless and even misleading. In practice almost the only lubricants which are tested for volatility are cylinder, superheated, and turbine oils, also transformer oils (see preceding Section, p. 43).

Volatility may be judged not only by the flashing point of an oil but also by its ignition point, i.e., the temperature at which the oil takes fire and burns steadily. Some authorities hold that this is an even better criterion of volatility than the flashing point.

(a) Evaporation or Volatility Test.

The volatility of a mineral lubricating oil is ascertained by determining the loss in weight it undergoes at a given temperature. Several special forms of apparatus have been constructed for this purpose.

1. **L. Archbutt's Vaporimeter.**[2]—This consists of a straight copper tube 1-2 ft. in length, having a branch tube attached at one end and coiled round it as shown in Fig. 27. The tube and coil are placed

[1] *J. Soc. Chem. Ind.*, 1891, **10**, 347.　　[2] *Ibid.*, 1896, **15**, 326.

in an air-oven provided with a thermometer; the ends of the tube are closed by brass screw-caps, one of which is provided with an exit-tube. The sample of oil is placed in a platinum boat which is placed in a glass carrier. The current of air in which the drying is effected is first heated to the required temperature in the coil before entering the actual drying tube, whereby a constant temperature is ensured; it is maintained at a constant speed by means of a suitable regulator.

The sample is exposed to the current of air for exactly one hour; 0·5 g. of oil is taken for each determination, and the temperature of the oven is varied to suit the requirements of the test. For cylinders working at 150 lbs. pressure per square inch, the oil is tested at 370° F.
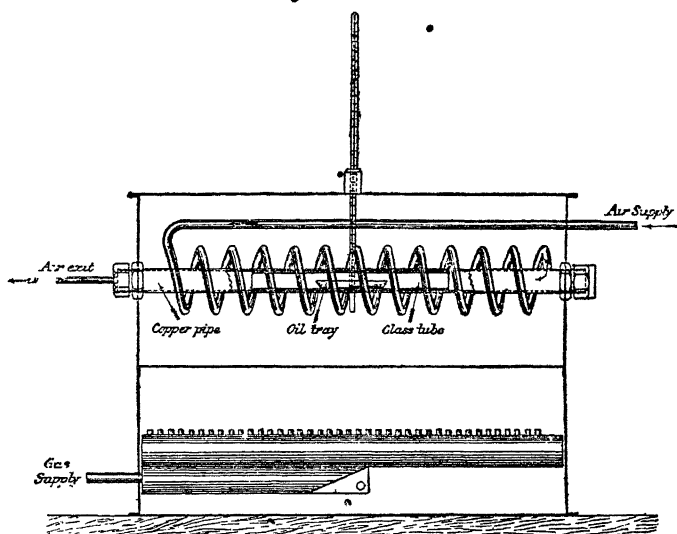
FIG. 27.

(188° C.), and should not lose more than 0·5-1·0 per cent. in weight. At 400° F. (=235 lbs. pressure) the loss of weight of cylinder oils is about two and a half times as great as at 370° F.

A flashing point apparatus in use in the United States, known as the **New York State Board of Health Tester,** is so fitted as to allow of the determination of the evaporation loss as well as of the flashing point. The outer bath of the tester is charged with water, whilst a known weight of the oil under examination is placed in the usual container. By keeping the water boiling, the oil is maintained at 208°-210° F. (about 98°·5 C.) during five hours, whereupon it is rapidly cooled to about 10° F. (5°·5 C.) and again weighed. Under these conditions a good machinery oil ought not to lose more than 0·1 per cent. The apparatus is apparently not intended for determining evaporation losses at higher temperatures.

2. F. Schreiber's Apparatus.[1]—This is a modification of the apparatus designed by Holde for the determination of the volatility, the object of which is to obtain indications of the actual efficiency of a lubricant under working conditions.

The oil to be tested is spread out in a thin layer and is uniformly heated from all sides, as in the cylinder of the steam engine.

The oven (Fig. 28) consists of a heating jacket in which high-boiling compressor oil is heated by a Bunsen burner. If the gas pressure is constant, the variations of temperature do not exceed ± 2°. The oils are placed in shallow glass dishes of 80-85 mm. diameter and 20 mm. deep, which are placed on a perforated shelf in the middle of the oven. The top of the oven has six openings to allow the vapour to escape, or to allow steam or gases to be passed through the oven in case it is not desired to carry out the test in air. 10 g. of the oil are weighed out into each of the dishes and heated for ten to twenty-four hours at 200°. The loss of weight by evaporation, and the increase of the amount of substances insoluble in benzine and benzene are ascertained. It has been found that in the case of oils which have not proved efficient under practical conditions, both of these amounts are high (Oils I. and II. in Table 17). Specific gravity, viscosity, and flashing point do not always give reliable indications of the volatility, as is shown by a comparison of the samples II. and V. in the subjoined Table, which have the same flashing point and specific gravity, but which gave very different losses on heating, viz., 8·78 per cent. in the case of II. and only 1·35 per cent. in the case of V. The results obtained in the case of five mineral oils are shown in Table 17; of these the two first proved unsatisfactory under working conditions.

Table 17.

Oil number.	I.	II.	III.	IV.	V.
Specific gravity	0·904	0·905	0·906	0·916	0·908
Viscosity { at 100° . . .	...	...	6·24	6·32	7·00
{ at 150° . . .	2·05	2·30	2·34	2·34	2·51
Flashing point } in open { .	317°	331°	338°	319°	332°
Burning temperature } vessel { .	362°	372°	382°	374°	378°
Per cent. of { Insoluble in benzine	0·16	0·04	0·05	0·64	0·05
asphaltic { Insoluble in ether-	1·07	0·54	1·59	1·65	2·29
substances { alcohol .					
Loss on evaporation after 16 hours, per cent.	13·6	8·78	1·15	3·66	1·35
	at 250°		at 280°		
Asphaltic substances after heating insoluble in benzine, per cent. .	10·8	5·13	1·26	1·84	1·28
Insoluble in hot benzene after heating	mostly insoluble	4·04	1·02	1·46	0·98
Other characteristics . . .	oil was solid and resembled parchment	oil was a tough doughy mass	liquid, without appreciable change		

[1] Z. angew. Chem., 1910, 23, 99 ; J. Soc. Chem. Ind., 1910, 29, 202.
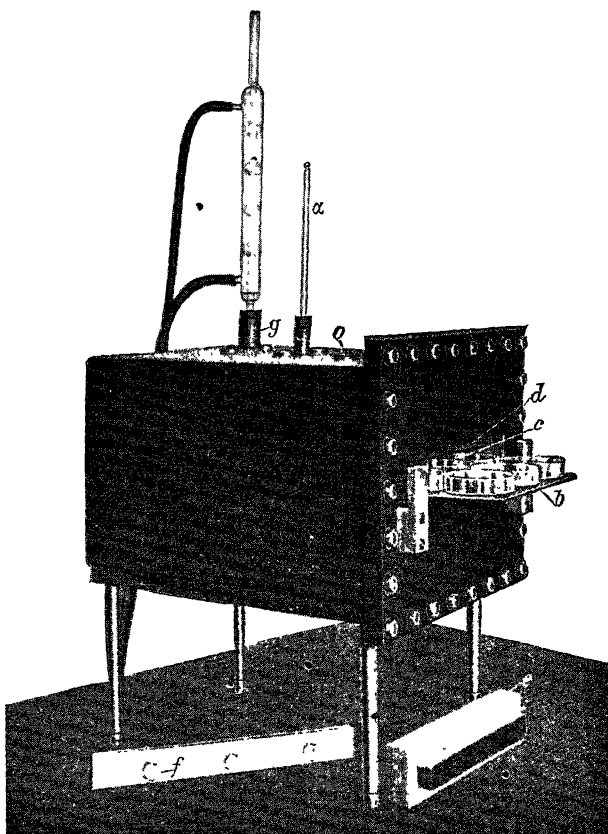
FIG. 28.

The great increase of asphaltic substances is due to oxidation, as was proved by the influence of steam and gases on the evaporation and character of the oil. A certain amount of formation of asphaltic compounds occurred even on heating in steam or carbon dioxide, but this may. be ascribed to the presence of small quantities of oxygen ; at any rate it was much less than when the oil was heated in air. A mineral oil containing 0·07 per cent. "insoluble" in benzine gave the results shown in Table 18.

Table 18.

Results of evaporation.	In a current of air.	In a current of carbon dioxide.	In a current of steam.
Quantity evaporated in 24 hours at 280° .	19·15	5·30	15·31
Insoluble in benzine, per cent. . . .	15·10	0·99	0·16
Insoluble in hot benzene, per cent. . .	13·53	0·23	completely soluble
Other characteristics	the oil formed a solid parch-ment-like mass	the oil was liquid without appreciable change	

(b) The Flashing Point.

The "Open" Test.—In the ordinary method of conducting this test the oil is simply heated up in an open crucible, in which a thermometer is placed, in a flat sand-bath and the temperature observed at which an inflammable vapour is given off. Owing to its simplicity this test is still largely accepted for railways, etc., and is in common use in factories for purposes of works control, and in trade generally.

A modification of this test proposed by J. Marcusson consists in applying the mechanical arrangement used in the Abel apparatus (see section on "Mineral Oils," this Vol., p. 29) for approaching the flame to the surface of the heated oil.

The Pensky-Martens Apparatus (Fig. 29).—Whereas determinations by the open test are subject to many uncertainties, and there is great difficulty in preventing the dissipation of vapour over the oil-surface, this apparatus is fitted with devices which ensure even heating, convenient approach of the igniting flame, and ready observation of the flash. A further advantage of the Pensky tester is that it gives results with low-flashing oils which stand in definite relation with the results by Abel's apparatus. As compared with the "open test," it is very sensitive to minute quantities of low petroleum fractions in otherwise high-flashing oils, the vapours of the former, which would simply escape in the open test, being detected by a low flashing point.

The oil to be tested is poured up to a mark M into the container E, which stands 34 mm. high, and is heated by a triple burner. E rests,

with an air-space interposed, in the iron bath H, which is protected against radiation by an asbestos-lined brass mantle L. When the temperature of the oil has risen to about 100°, the hand-worked stirrer J is brought into operation, and is kept agitating without interruption until the end of the test. Fig. *b* is a cross section of the cover and Fig. *c* a holder for removing the hot container. From 120° onward the
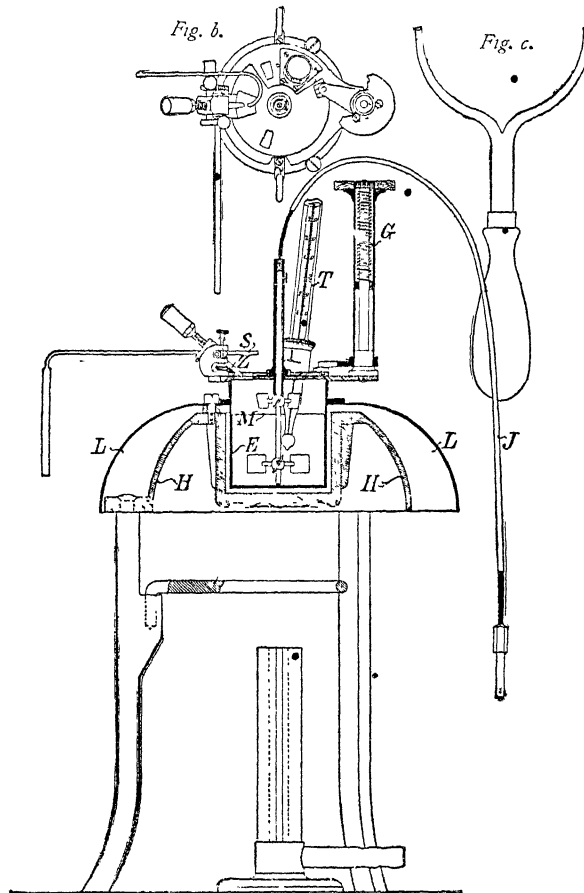
FIG. 29.

ignition flame Z, burning gas or colza oil, is plunged into the upper part of E at intervals of 2°; later on, when the flame is seen to increase in size on insertion, it is applied at one-degree intervals, until flashing sets in. The temperature read on the thermometer *T* may be corrected for the errors of the instrument itself, and for the column of mercury protruding above the heated region. Not infrequently the flash extinguishes the ignition flame. On immediately again introducing the flame, the same flashing point need not necessarily be observed, since

further heating may be requisite to collect a sufficiency of inflammable vapour.

The heating should be so controlled that, with continual agitation, the temperature rises 6°-10° per minute up to 120°, and only 4°-6° per minute from about 20° below the flashing point.

It rarely happens that the flashing point of a lubricating oil falls below 120°, but when this is the case, stirring should be begun at 80°, and the insertion of the ignition flame at 100°. In order to rekindle the latter when it goes out, a stationary flame S is kept burning near it.

Repeated determinations usually agree to within 0°-2°; the difference rarely amounts to 3°. Two determinations, of which the mean is taken, are therefore, in general, sufficient.
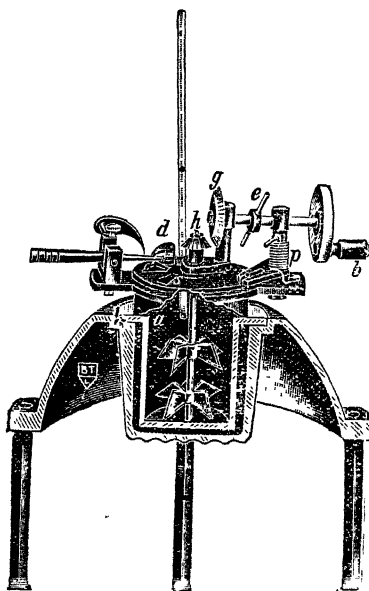
FIG. 30.

Much less concordance may be expected when the oil consists of a mixture of mineral oils and glycerides.

A sample of oil which has once undergone a flashing test should not be used for a repetition of the same, since it has necessarily lost some of its most volatile constituents.

When an oil containing water is heated in the Pensky apparatus the steam spasmodically generated has the effect of blowing out the ignition flame. If serious trouble be experienced from this cause, it is well to dry the oil beforehand by treatment with calcium chloride and filtration. There is no difficulty in distinguishing the blowing out of the flame by steam from that which takes place in the neighbourhood of the flashing point.

If lubricants should contain lamp oil, and hence flash too low to be dealt with by Pensky's apparatus, the Abel tester may be used (see p. 29).

J. Gray's Apparatus.[1]—This apparatus is frequently used in this country for the determination of the flashing point of heavy mineral oils. A section of the cup and surrounding iron jacket is shown in Fig. 30, and the complete apparatus in Fig. 31. The cup a which is
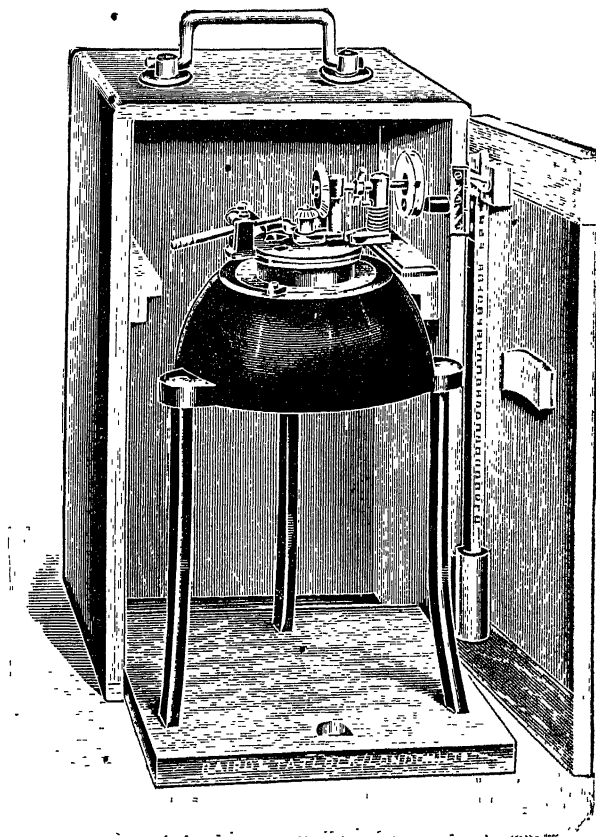
FIG. 31.

made of brass is closed by a tightly fitting lid, through the centre of which passes a steel shaft carrying two sets of stirrers, one above and the other below the surface of the oil. A small bevelled wheel h is fixed on the top of the shaft and geared with the vertical wheel g which is worked by the small handle b. The lid is provided with four openings, one of which serves for the insertion of a thermometer, whilst the other three serve for the mechanism provided for the testing of the flashing point.

[1] *J. Soc. Chem. Ind.*, 1891, **10**, 348.

To carry out the test the cup is filled with the oil up to a mark inside which is $1\frac{1}{2}$ in. from the bottom, the test-lamp lighted, and the flame adjusted so that it is about $\frac{1}{8}$ in. high. The oil-cup is then heated, either by means of a Bunsen burner or on a sand-bath, the stirrers being rotated so that the temperature of the oil rises about 5° per minute at first, and then less rapidly as the flashing point of the oil is approached; it is important not to work the stirrers too rapidly as otherwise oil is sent up the side of the vessel, whereby the ratio of the surface of oil exposed to the air space is increased, with the result that the observed flashing point may be 2° to 3° too low. The mechanism of the apparatus is then brought into play, whereby the stirring of the oil is stopped, the cover of the cup opened, and the test-lamp tilted into the opening over the cup. The temperature at which a slight explosion is produced is taken as the flashing point of the oil. If there is no flash the heating is continued as before and the test repeated.

Differences between the Flashing Points by the "Open" and "Closed" Tests.—In the "open" test vapours arising from the oil are soon carried away by atmospheric convection currents, whereas this cannot occur to any extent in the Pensky - Martens or in Gray's apparatus. Consequently the flashing points always come out higher by the latter than by the former method. With ordinary mineral lubricants the differences range from 5°-40°, according to the flashing point.

(c) The Ignition Point.

The ignition point or "Fire Test" is the lowest temperature at which the oil will continue to burn after a flame has been brought into contact with its surface for a few seconds. It is determined after the flashing point has been taken by removing the cover, continuing the heating, and testing with a small flame.

VII. OPTICAL TESTS.

Optical Activity.

Certain crude petroleums and the fractions distilled from them slightly rotate the plane of polarisation. Rosin oils, on the other hand, exhibit considerable rotations.

Mineral oils have specific rotatory powers of 0 to $+1°\cdot2$ rarely rising to $+3°\cdot1$. The rotation of rosin oils fluctuates between $+30°$ and 44°. (Demski-Morawski records $+50°$.) Fatty oils do not appreciably rotate the plane of polarised light, with the exception of sesame oil, which has a specific rotation of from $+3°\cdot10$ to 9°, castor oil, which has a rotation of from $+40°\cdot7$ to $+43°$, and some rarer oils and fats.

III F

The rotatory power is determined with the usual polarimetric apparatus. Strongly coloured oils are first dissolved, in known concentration, in a colourless, inactive mineral oil, or in petroleum spirit or benzene.

If $[a]_D$ be the specific rotation of the substance, the formula for calculation in the case of the original oils is :—

$$[a]_D = \frac{a}{l \times d}$$

and in the case of solutions :—

$$[a]_D = \frac{100 \times a}{l \times p \times d}$$

where a is the angle of deviation read off on the polarimeter, l the length of the column of liquid, d the specific gravity of the oil or of the solution, and p the percentage concentration of the latter.

Refractivity.

The refractive index permits of the detection of rosin oil in lubricants. Zeiss' refractometer (see section on "Oils, Fats, and Waxes," this Vol., p. 109), is the most serviceable instrument for the determination.

The refractive index of high-boiling rosin oils is from 1·530-1·550; that of mineral lubricating oils from 1·490-1·500; that of colza oil from 1·472-1·474; and that of neat's-foot oil from 1·467-1·470, all at 18°.

CHEMICAL TESTS.

VIII. ACIDITY AND FREE ALKALI.

In pale refined mineral oils there is no free acid, or at most traces (up to 0·03 per cent., calculated as SO_3) may occur. Dark oils may contain up to 0·3 per cent., although their normal acidity may be taken to be 0·15 per cent. or less; if waste oils have been added the acidity may rise up to 0·5 per cent. The acidity is due either to resinous substances or to naphthenic acids of uncertain molecular weights; the acidity is expressed either in terms of SO_3 or as the "acid value." For lubricants the acidity is stated on the Continent in terms of SO_3, i.e., the number of grams of SO_3 equivalent to the potassium hydroxide required for the neutralisation of the free acids in 100 g. of the oil. The "acid value" represents the number of milligrams of potassium hydroxide required for the neutralisation of 1 g. of the oil. 1 per cent. SO_3 is equivalent to an acid value of 14 (=7·05 per cent. oleic acid).

Free sulphuric acid and free alkali due to traces of these substances

left from the refining processes are very rarely met with in lubricants; they are detected and determined in the usual manner after extraction with hot water. The acidity of oils is determined by titrating either their ether-alcoholic solutions or their alcoholic extracts.

Pale Oils.—For the estimation in this case 10 c.c. of the sample are washed with 150 c.c. of a neutralised mixture of two parts of absolute alcohol and one of ether into a flask which already contains a little of the same mixture. 1 c.c. of 1 per cent. alcoholic solution of phenolphthalein is added, and the titration is carried out with standardised alcoholic sodium hydroxide solution of such a strength that 1 c.c. corresponds to 0·004 g. SO_3 (*i.e.* decinormal).

Dark Oils.—In this case 20 c.c. of oil are well shaken, after warming, if necessary, in a stoppered measuring cylinder with 40 c.c. of neutralised absolute alcohol. The liquid is allowed to settle over night, and 20 c.c. of the alcoholic layer are then withdrawn with a pipette, and titrated as described above. If the acidity exceeds 0·03 per cent., the alcoholic liquid is poured off and the oil shaken up once or twice with a fresh 40 c.c. of alcohol, and again titrated.

The Detection of Mineral Acid is confined to sulphuric acid. About 100 c.c. of oil are shaken with twice the volume of hot distilled water in a capacious flask; after the two layers have separated, 20-30 c.c. of the aqueous extract are withdrawn with a pipette, filtered clear, and tested with a drop of methyl orange solution (0·3 g. per litre). Further portions of the aqueous extract may be tested for added glue, soap, salt, etc. (see p. 95).

Mineral oils thickened with soap yield emulsions which refuse to separate into two layers; these emulsions invariably show a decided alkaline reaction.

In the case of mineral oils (especially those intended for compressors) which are artificially coloured with coal-tar dyes, the disturbing influence of the dyestuff may be obviated by proceeding in one of the following ways:—

α. If the dyestuff is soluble in hydrochloric acid, a solution of the oil in petroleum spirit is shaken repeatedly with dilute hydrochloric acid; this is then removed by thorough shaking with water. The decolorised solution is then titrated as above.

β. If the dye is insoluble in acid, the oil is first treated with tin and hydrochloric acid, whereby the colouring matter is, as a rule, reduced to the leuco-base or other colourless derivative. The decolorised oil is then dissolved in petroleum spirit, washed free from acid, and titrated.

γ. A solution of the oil in petroleum spirit is shaken with a measured quantity of $N/10$ alcoholic sodium hydroxide (containing about 50 per cent. of water). The whole of the liquid is then titrated, using phenolphthalein as the indicator, until the aqueous layer is

colourless. The total acid required is subtracted from the amount corresponding to the sodium hydroxide added; the difference represents the acidity of the oil.

δ. If the dyestuff is insoluble, or nearly so, in alcohol, it is often possible to extract the oil with hot 80 per cent. alcohol; the (almost) colourless extract can then be fitrated.

Oils containing soap as well as colouring matter may be dealt with directly either by method γ or δ; but it is better, whenever possible, to free the oil from soap by extraction with petroleum spirit or anhydrous acetone.

Mineral acids can be detected just as easily in dyed as in undyed oils by means of methyl orange, since the dyestuffs do not pass into aqueous solution.

In dyed oils which contain *Fatty Admixtures*, the determination of acidity may be conducted by methods α, γ, or δ. Method β is inadmissible, since the fatty matter may become hydrolysed by concentrated hydrochloric acid.

Thus the acidity in a blue-black leather grease, consisting of waxes, oil of turpentine, and dyed with nigrosine, was determined by boiling up 5 g. of the grease with petroleum spirit, allowing to cool, and filtering; this operation was repeated several times. Most of the dye remained in the residue, the solutions being only slightly coloured. They were then repeatedly extracted with dilute hydrochloric acid, washed thoroughly with water, and titrated.

Differentiation of Naphthenic and Fatty Acids.—To ascertain whether the free acids present in an oil are naphthenic or fatty acids, Davidsohn[1] has recourse to the solubility in water of the alkali-earth salts of the latter. The alkali-soap is dissolved in water, an excess of a 10 per cent. magnesium chloride solution added, the whole boiled, and the precipitate filtered off. The filtrate is concentrated on the water-bath, and treated with a few drops of hydrochloric acid, when the presence of naphthenic acids is indicated by the solution becoming strongly turbid.

IX. ROSIN IN LUBRICATING OILS.

Qualitative Detection.—The presence of rosin in mineral oils is indicated by high acidity. An acidity of 1 per cent. of SO_3, or an acid value of 14, corresponds to about 9 per cent. of rosin (colophony). Rosin is characterised by an acid value of from 146-170, a saponification value of from 167-194, and an iodine value of from 100-125.

In order to isolate the rosin, the oil is thinned with petroleum spirit and extracted repeatedly with dilute sodium hydroxide solution. From

[1] *Seifensieder Zeit.*, 1909, Nos. 51 and 52.

this solution the rosin is separated by mineral acid. It is identified by the above characteristics, its specific gravity, and by means of the Liebermann-Storch colour reaction (see "Detection of Rosins in Oils," this Vol., p. 130). For this test the substance is dissolved in a little acetic anhydride, and a drop of sulphuric acid of sp. gr. 1·53 added; colophony gives a violet coloration.

The Quantitative Determination of Rosin.—If fatty oils and fatty acids are absent, this is effected by extracting the oil with sodium hydroxide solution, acidifying the solution, and weighing the separated rosin; when fatty matter is present as well as rosin, the separated mass contains both. The rosin is then separated from the fatty matter by Twitchell's process (see "The Determination of Rosin in Soap," this Vol., p. 195).

For this purpose so much oil is weighed or measured out that about 5 g. of rosin and fatty acids will be obtained. The mixture is saponified by means of alcoholic alkali, and the soap solution thus obtained is freed from unsaponifiable matter by extraction with ether or petroleum spirit, and is then evaporated to dryness; the residue is taken up with water, acidified with hydrochloric acid, and extracted with ether. The aqueous liquid is again neutralised, evaporated to about 25 c.c., acidified, and again extracted with ether. The combined ethereal extracts are then evaporated down. The residue is then subjected to the Twitchell process as described under "Soap," this Vol., p. 195.

X. LIABILITY TO "GUM" OR "RESINIFICATION" OF LUBRICANTS.

Pale mineral oils, on exposure in thin layers, volatilise almost completely at 100° within thirty-five hours.

Dark oils containing still residues scarcely thicken at ordinary temperatures, even after a very long time; but at 50°-100° they are apt to resinify to a considerable extent, since the more volatile hydrocarbons partly evaporate off and partly become oxidised, leaving a residue of pitch-like bituminous matter.

In order to test an oil in this respect, a drop is allowed to spread on a sheet of glass 5 by 10 cm., and kept at 50° for machinery oils, or at 100° for cylinder oils; from time to time, say once a day, the sample is cooled down and its consistency noted.

In consequence of the modern method of ring-lubrication and the mode of lubrication of turbine engines, where the same oil remains for a long time on the bearing, the requirements of the user, as regards liability to gumming of oils, especially of oils subjected to high temperatures for considerable periods, have become much more stringent than formerly, when the oil used for lubrication ran away. Hence more

searching methods of determining the liability of an oil to undergo change are required.

R. Kissling[1] has proposed to determine the "tar number," the "coke number," the "tar formation number," and the "coke formation number," as a means of examining lubricants from this standpoint. The "tar number" is the term he applies to the percentage content, which can be extracted from the oil with hot alcoholic sodium hydroxide at 80°, and after acidification can be extracted from this solution with benzene. The "coke number" is determined on the residual oil after extracting the "tar," and is the quantity of "coke-like substances" insoluble in petroleum spirit. If the oil is heated for fifty hours to 150°, and the "tar" and "coke" numbers are again determined as described, the quantities obtained are termed the "tar formation number" and "coke formation" number respectively.

As Kissling's proposals have not yet been adopted by other workers, it will suffice to record the following results :—

Pennsylvanian oils.	Sum of tar and coke formation numbers	.	0·2 to 0·5
Russian oils	„ „ „	.	1·2
Texas oils	„ „ „	.	2·2 to 2·8

The higher these numbers in an oil, the more rapidly it is found to undergo changes in practical use.

XI. FORMOLITE REACTION (A. NASTJUKOFF'S TEST).[2]

For the determination of the unsaturated cyclic hydrocarbons in a mineral oil, Nastjukoff treats the oil with formaldehyde in presence of concentrated sulphuric acid, whereby a solid yellow product is separated for which the name "formolite" has been proposed. The "formolite-number" is the amount of air-dry "formolite" obtained from 100 g. of an oil.

The test is carried out by adding 30 c.c. of concentrated sulphuric acid to the same quantity of the oil, and then, without shaking, adding 15 c.c. of a 40 per cent. formalin solution, whilst cooling the mixture. When this has cooled to the ordinary temperature, it is poured into water, neutralised with ammonia, filtered off on a Buchner funnel, and washed, first with petroleum spirit or ether, and then with hot water. After drying in an oven at 110°-115° the product is bright yellow to dark brown in colour, amorphous, and, according to Nastjukoff, insoluble in the usual solvents; V. F. Herr, however, found it to be distinctly soluble in a large quantity of hot chloroform (1 : 100), and has suggested applying the test directly to crude oils without previously

[1] Chem. Zeit., 1906, 30, 932; 1907, 31, 328 ; 1908, 32, 938 ; and 1909, 33, 521.
[2] Petroleum, 1909, 4, 1336, 1397.

treating the oils with sulphuric acid, as Nastjukoff does. Herr obtained the following values :—

Table 19.

Crude oil from	Formolite number.
Binagdy	63·3
Bibi-Eybat	28·3
Balachany	21·3

These figures correspond to the chemical behaviour of the oils, as the Balachany oil is the richest in naphthenes, and the naphthenes do not yield "formolite." This reaction furnishes valuable practical information as to the working up of crude naphtha.

The formolite numbers of various American and Russian lubricating oils (cylinder oil, machine oil, spindle oil, vaseline oil), given by Nastjukoff,[1] show that all these oils consist essentially of unsaturated cyclic hydrocarbons. Thus American cylinder oils gave formolite numbers of 92-97, Russian cylinder oils of from 58-87, and vaseline oils of from 7·8-22.

Herr[2] has recently pointed out that formalin may be advantageously replaced by methylal $CH_2(OCH_3)_2$, as the latter acts at the same time as a solvent for the oil, and as a condensing agent, and, moreover, forms a better condensing agent for the detection of benzene hydrocarbons than does formaldehyde.

XII. BEHAVIOUR TOWARDS METALS.

Corrosion of bearings by machinery and axle oils never takes place to an appreciable extent at ordinary temperatures, unless fatty oil containing free acid is present. Comparative tests, carried out first by I. I. Redwood,[3] may be made by immersing polished and weighed plates of the metal concerned, 30 or 50 mm. square, in the oil contained in glass or porcelain basins, and heating them, protected from dust, in an air-bath. From time to time during the period of the test, which may be continued for weeks, the plates are cleaned with tissue paper and ether, inspected, and weighed. It must, however, be pointed out that these tests by no means furnish reliable guidance as to the behaviour of the oils on a practical scale.

XIII. MOISTURE.

Qualitative Detection.—The presence of moisture in pale oils is usually indicated by a more or less pronounced cloudiness, especially

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[1] *Petroleum*, 1909, 4, 1336, 1397.
[2] *Chem. Zeit.*, 1910, 34, 893 ; *J. Soc. Chem. Ind.*, 1910, 29, 1094.
[3] *J. Soc. Chem. Ind.*, 1886, 5, 362.

after the sample has been shaken. By heating on the water-bath, the oil loses its cloudiness, which differentiates it from the cloudiness caused by the separation of paraffin wax, etc.

Quantitative Determination.—From 10-12 g. of the sample are weighed into an open glass or porcelain dish of 6-10 cm. diameter; if much moisture is present, 3-5 g. are weighed out and mixed with 10-15 g. of the same oil, previously dehydrated with calcium chloride and filtered. The dish is heated on a briskly boiling water-bath until no more froth is formed, when the oil is stirred with a glass rod. Side by side another sample, but which has been previously dehydrated, is treated in exactly the same way. The percentage loss in weight of the latter is subtracted from that of the former; the difference represents the moisture in the original sample. In the case of practically non-volatile cylinder oils, the blank test may be omitted.

XIV. MINERAL ASH.

No ash is obtainable if the oil is completely soluble in petroleum spirit and benzene, and the aqueous and hydrochloric acid extracts of the oil give no perceptible residue on evaporation. Well-refined machine oils should not contain more than 0·01 per cent., and cylinder oils not more than 0·1 per cent. of ash, which should not, however, contain any appreciable quantity of alkali.

For the determination of the ash 20-30 g. of the oil are carefully evaporated in a platinum dish over a small flame, until the residue is solid; this is incinerated and the residual ash weighed. If the carbonaceous residue is difficult to burn off by simple heating, the combustion is assisted by adding ammonium nitrate.

XV. PRESENCE OF SOAP.

It has been pointed out above that solid lubricants contain alkali- or lime-soaps which are purposely added.

The presence of alkali-soap is indicated by the oil, on being shaken with water, giving an emulsion having an alkaline reaction to phenolphthalein.

After acidification with a mineral acid, sodium or potassium may be detected by the usual methods. The presence of ammonia-soaps is recognised by the smell of ammonia (see also p. 103). Lime- or alumina-soaps are best tested for in an acid extract of the oil.

Quantitative Determination.—For the quantitative determination of soap, use is made of the fact that, by agitating the sample with mineral acid, the soap is decomposed, its equivalent amount of free fatty acid

being dissolved by the oil, the total acidity of which is then greater by that amount than its original acidity. The nature of the soap-acids may be ascertained by isolating them and examining them according to the methods described in the following Section. The soap-bases are identified in the aqueous solution.

To carry out the determination 10 c.c. of the oil are dissolved in a separating funnel in 40-60 c.c. of ether. The solution is thoroughly shaken with so much dilute hydrochloric acid that the aqueous layer remains distinctly acid. The latter is separated off, and the residue repeatedly washed with water until free from acid. Any emulsions formed are broken by adding more ether or a strong solution of common salt, or a little alcohol, which is poured on without shaking.

If the emulsion persist, nevertheless, warm petroleum spirit is substituted for ether, and the solution washed with warm water. Separation having been effected, the ethereal solution is titrated for acidity as described on p. 82. Finally, the acidity of the original oil is determined; the difference between the two acidities corresponds to the amount of fatty acids present as soaps.

XVI. ADMIXTURES OF FATTY OILS.

To detect the presence of fatty oils rapidly, 3-4 g. of the sample are heated in a test tube with either sodium or sodium hydroxide for a quarter of an hour in a paraffin-bath, pale oils to 230°, dark and cylinder oils to 250°. In the presence of 0·5 per cent. of glycerides in pale oils, of 2 per cent. in dark oils, a formation of soapy froth will be observed, and the oil will gelatinise on cooling.

It should be pointed out, however, that gelatinisation may take place without frothing, if rosin and naphthenic acids are present.

Quantitative Determination.—The percentage of fatty oil is determined quantitatively by heating 10 g. of the sample for half an hour with 25 c.c. of $2/N$ alcoholic potassium hydroxide and 25 c.c. of benzene under a reflux condenser; 25 c.c. of water are then added, and the solution is washed into a separating funnel with 50 per cent. alcohol. The soap solution is shaken out several times with 50 c.c. of low-boiling petroleum spirit, until the last extract leaves no oily residue on evaporation. The united petroleum spirit extracts are shaken out three times successively, with 15 c.c. of 50 per cent. alcohol to which a trace of alkali has been added. This alcohol extract is shaken out once with petroleum spirit, and is then added to the soap solution. The petroleum spirit solutions are evaporated, and the residue heated on a water-bath until the solvent is driven off completely. After drying for five minutes at 100° the mineral oil thus obtained is weighed. The difference between the amount of mineral oil thus

found and the quantity of oil originally taken gives the content of saponifiable fat.

If approximate data suffice, it is simpler to determine the saponification value of the sample (see next section, "Saponification Value," p. 114).

For this purpose 4-10 g. of the oil are heated for half an hour under a reflux condenser with 25 c.c. of $N/2$ alcoholic potassium hydroxide, or, in the case of very thick oils, 25 c.c. of $N/1$ potassium hydroxide and the same volume of benzene. The excess of alkali is then titrated back with $N/2$ hydrochloric acid, using phenolphthalein as the indicator, and the saponification value calculated as described in the next Section, p. 115.

For the calculation 195 may be taken as a mean saponification value of the oils that come under consideration, with the exception of rape oils, for which 175 should be taken; the saponification value of mineral oil is, of course, nil. Hence, e.g., if the sample has the saponification value 97.5, the percentage of fatty oil, if rape oils be absent, is 50 per cent. Any alkali necessary to neutralise free acid in the oil (acid value) must, of course, be deducted from the saponification value, and the difference calculated to glycerides.

For exact determinations the fatty acids are separated and examined as described in the following Section, p. 130.

In the presence of wool grease (the saponification value of which is about 105), a complication arises owing to the higher alcohols of the wool grease remaining with the unsaponifiable mineral oil. In this case the latter is boiled, after removal of the soap solution, with an equal weight of acetic anhydride for two hours under a reflux condenser, whereby the alcohols are converted into esters. These remain dissolved in the warm acetic anhydride solution which is separated off; the mineral oil is then washed several times with a few cubic centimetres of warm acetic anhydride in a separating funnel. From 3-5 per cent. of mineral oil are lost in this process, and must be duly taken into account. Owing to the fact that wool grease itself contains hydrocarbons, and further that it is not completely saponified by boiling with alcoholic alkali, quantitative determinations of wool grease by the method described above, yield only approximate results.

The Identification of the Fatty Matter.—This is carried out by the methods described in the following Section, pp. 130 et seq.

XVII. ROSIN OILS AND TAR OILS.

Rosin Oils.—Heavy rosin oils, boiling above 300°, are produced by the destructive distillation of colophony, light rosin spirit or pinolin coming over in the first runnings.

Crude rosin oil is mainly a mixture of hydrocarbons (which consist, according to Bruhn and A. Tschirch,[1] principally of reduced retenes); according to the care with which it has been distilled it may contain up to 30 per cent. of rosin acids.

Crude and refined rosin oils find application as electrical insulators, and in the manufacture of lubricants, varnishes, and water-soluble oils.

Rosin oil dissolves in twice its volume of absolute alcohol to the extent of 50-100 per cent., in mineral oils to 2-15 per cent., and in very light mineral oils to 35 per cent. It is miscible in all proportions with acetone, whereas mineral oils require several volumes for complete solution.

The refractive index of rosin oils is 1·535-1·550 at 18°, that of mineral oils 1·490-1·507. The specific gravity varies from 0·880-0·915. Rosin oils are strongly optically active: $[\alpha]_D$ ranges from $+30°$ to $+50°$; mineral oils, on the other hand, are as a rule inactive, or at most have $[\alpha]_D = +3\cdot1.$[2]

The iodine value of rosin oils varies from 43-48. It may be pointed out that cracked petroleum distillates have iodine values, sometimes reaching 70.

When a few cubic centimetres of rosin oil are shaken with an equal volume of sulphuric acid of sp. gr. 1·6, a deep red colour results. This colour reaction is due to impurities which are absent from well-refined rosin oils, such as are now placed on the market.

On adding to a mixture of 1 c.c. of oil and 1 c.c. of acetic anhydride a drop of sulphuric acid of sp. gr. 1·53, a fine violet colour is produced (Liebermann-Storch reaction, see p. 130). This reaction is given by rosin as well as by rosin oil. When both are present together rosin oil may be detected by its odour, and by the further characteristics described below.

· If a lubricating oil is suspected of containing rosin oil, the examination must be based on the properties described above; if necessary, the tests are performed on that portion of the lubricant which is soluble in absolute alcohol in which the rosin oil is much more soluble than the mineral oil.

Determination of Rosin Oil in Mineral Oils.—The best method for this determination is that of E. Valenta, which is based on the difference in the solubilities of rosin oils and mineral oils in glacial acetic acid at 50°; 10 c.c. of glacial acetic acid dissolve 1·7788 g. of the former, and from 0·2833-0·6849 g. of the latter.

For the determination, 2 c.c. of the unsaponifiable matter are mixed in a test tube with 10 c.c. of glacial acetic acid, and the tube, loosely closed by a cork, is immersed in a water-bath at 50° for five minutes

[1] *Chem. Zeit.*, 1900, **34**, 1105 ; *Arch. Pharm.*, 1903, **291**, 523.
[2] Rakuzin, *Chem. Zeit.*, 1904, **38**, 574.

the contents being frequently shaken. The mixture is then filtered through a moistened filter, and the middle portion of the filtrate collected. Part of this is then weighed off accurately, and the content of acetic acid determined by titration with $N/1$ sodium hydroxide. The difference between the weight of the acid taken and the weight thus found corresponds to the quantity of rosin oil dissolved.

The accuracy of this method has been confirmed by J. H. Walker and C. D. Robertshaw.[1]

Rosin acids, if present in the rosin oil, influence the solubility, and render the determination inaccurate. In this case, the greater part of the acetic acid is neutralised, the solution diluted with water, and the rosin oil extracted with ether.[2]

According to the method due to L. Storch,[3] which applies only in absence of fatty oils, 10 g. of oil are well shaken with five parts of warm 96 per cent. alcohol. After cooling, the alcoholic solution is separated off, and the residue washed with a small quantity of the solvent. The combined solutions are evaporated in a tared conical flask and heated on the water-bath till free from alcohol. The weighed residue (A) is then treated with ten parts of alcohol, and the substance dissolved is again isolated and weighed (B). There will still be some mineral oil in B, and its amount is calculated as follows:—Suppose a grams of alcohol to have acted upon the original material, and b grams upon A; then a-b grams dissolve A-B grams of mineral oil; therefore b grams dissolve $\dfrac{(A\text{-}B)\ b}{a\text{-}b}$ grams of the same. This latter amount is worked out and subtracted from B, and thus gives the quantity of rosin oil in the original 10 g. of mixed oil.

Detection of Mineral Oil in Rosin Oil.—Mineral oils afford no very characteristic qualitative reactions, and when there is less than 15 per cent. in a sample of rosin oil, no information can be gained by the ordinary solubility methods. Holde's procedure for detecting small admixtures of mineral oil is based on differential solubilities and on differential refractivities. According to this method 10 c.c. of oil are shaken up with 90 c.c. of 96 per cent. alcohol at the ordinary temperature. If any considerable amount of oil remains undissolved, the presence of much mineral oil is indicated. In this case the insoluble oil is allowed to settle out overnight, rinsed with alcohol, and tested by the refracto-meter. A refractive index of less than 1·533 at 18° is evidence of mineral oil.

Heavy rosin oils lose much more weight at 100° and 180° than mineral oils, even than light spindle oils. Similarly the flashing point

[1] *Analyst*, 1902, **27**, 238.

[2] A. H. Allen, *Commercial Organic Analysis*, 2nd ed., vol. ii., p. 465.

[3] *Ber. Österr. Gesell. z. Förder. der Chem. Ind.*, 1891, **9**, 93 ; *J. Soc. Chem. Ind.*, 1891, **10**, 276.

of rosin oil is relatively lower. The following Table affords some guidance for examination :—

Table 20.

| | Loss on heating (per cent). | | Flashing point. | |
	For 5 hours at 100°.	For 2 hours at 170°.	Pensky.	Open test.
Heavy rosin oil . .	0·4 to 0·8	5·6 to 7·4	109° to 146°	148° to 162°
Spindle oil . . .	0·05 „ 0·10	0·5 „ 1·8	177° „ 203°	189° „ 213°
Machinery oil . . .	0·06 „ 0·13	0·6 „ 1·05	188° „ 195°	205° „ 221°

Coal-tar Oils.—The oils which come under consideration here and which are used as lubricants in gas-suction pumps and as ingredients of lubricating greases, are the dead anthracene oils, heavier than water, and having a characteristic smell of creosote. They are completely soluble in alcohol at the ordinary temperature, and are dissolved by concentrated sulphuric acid on the water-bath forming compounds soluble in water. With nitric acid of sp. gr. 1·45 they yield nitro-products with evolution of heat and sometimes with almost explosive violence. The following method for their determination, which gives approximate results, has been based on the rise of temperature produced by this treatment :—7·5 c.c. of the sample are placed in a graduated tube, cooled to 15°, and 7·5 c.c. of nitric acid of sp. gr. 1·45, previously cooled to 15° added ; the tube is closed by a cork provided with a thermometer, the contents thoroughly shaken, and the rise of temperature read off. It is well to try a preliminary test always, in order to ascertain whether a violent reaction takes place or not, as a guide to the quantity of the sample to be taken, and the size of the tube to be employed for the test.

For the differentiation of coal-tar oils from mineral oils the reaction proposed by E. Valenta[1] may be used. This depends upon the solubility of benzene hydrocarbons as found in coal-tar in dimethyl sulphate ($SO_2(OCH_3)_2$) at the ordinary temperature, and the insolubility of crude petroleum, benzine, illuminating oil, mineral oil, and rosin oil. A certain quantity of the oil is shaken for a minute in a measuring cylinder with $1\frac{1}{2}$-2 vols. of dimethyl sulphate and allowed to separate, whereupon the difference of volume is read off.

This method has been tested by E. Graefe,[2] who found that it gave almost theoretical values in the case of mixtures of high-boiling coal-tar and mineral oils, but that in the case of very low-boiling petroleum derivatives, the solubility in dimethyl sulphate is appreciable. In

[1] *Chem. Zeit.*, 1906, **30**, 266 ; *J. Soc. Chem. Ind*, 1906, **25**, 366.
[2] *Chem. Rev. Fett-Ind.*, 1907, **14**, 112.

lignite-tar oils a constant error of approximately 10 per cent. occurs; but if this be taken into account, the separation of coal-tar and lignite-tar oils can be effected by this method. The method has also been examined by T. W. Harrison and F. M. Perkin,[1] who found that aromatic oils are soluble in dimethyl sulphate in all proportions, but that mineral oils are not insoluble. Thus 8·5 per cent. of Russian petroleum was dissolved by its own volume of the reagent, and by repeated extraction with fresh quantities as much as 80 per cent. could be dissolved. Hence it is concluded that the method cannot be applied quantitatively, although of value as a qualitative test.

Heavy Lignite Oils (*cf.* the section on "Mineral Oils," p. 53) have a sp. gr. of 0·89-0·97, and dissolve to the extent of 20-60 per cent. when shaken with 2 vols. of cold alcohol; the viscosity is usually low. These oils have a faint smell of creosote; their properties are, on the whole, not sufficiently well-marked to render them certain of detection.

XVIII. INDIA RUBBER.

The presence of india rubber in lubricating oils may be recognised by their tendency to run into threads when drawn out by a glass rod, or between the fingers. A rough determination of the india rubber may be effected by dissolving the oil in ether and precipitating with absolute alcohol. If present in a homogeneous dissolved condition, india rubber may be regarded as a perfectly harmless ingredient, since it neither attacks metals nor tends to thicken; it has the effect of rendering the oil peculiarly slippery and adhesive.

As yet there is no standard method of determining the amount of india rubber in lubricating oils. Methods based on the formation of addition products, insoluble in acetone, either with nitrous acid or with hyponitrous acid, have not yet been worked out for the estimation of india rubber in oils.

XIX. DEBLOOMING AGENTS AND PERFUMES.

Mono-nitronaphthalene, $C_{10}H_7NO_2$, is added to mineral oils to mask the fluorescence, whilst the presence of an objectionable smell is overcome by the addition of nitrobenzene. The latter is recognised at once by its characteristic odour of bitter almonds. Yellow coal-tar dyes, which are also used similarly to nitronaphthalene, are indicated by their deep yellow colour. Oils treated with nitronaphthalene become darker on keeping.

Detection of Nitronaphthalene.—As a preliminary test from 1-2 g. of the oil are boiled with 2-3 c.c. of concentrated alcoholic potassium

[1] *Analyst*, 1908, **33**, 2.

hydroxide (about $2/N$) in a test tube for a minute or two. In the presence of nitronaphthalene or nitrobenzene the liquid becomes blood-red or even violet, owing to the formation of azo-compounds. The reaction is especially well observed when drops of the liquid adhering to the upper part of the test tube are gently warmed.

If the colour test has given a positive indication, the following confirmatory test proposed by N. Leonard may be applied.[1] A few cubic centimetres of the oil are placed in a conical flask, and reduced by warming with tin and hydrochloric acid for five to ten minutes. A piece of platinum wire may with advantage be placed in the liquid. The acid aqueous solution is separated from the oil, filtered into a separating funnel, and treated with sufficient potassium hydroxide to neutralise the acid and redissolve the stannous hydroxide precipitate. The presence of nitro-naphthalene in the original oil is indicated by the characteristic unpleasant smell of α naphthylamine. This is extracted with 10-20 c.c. of ether and the ethereal solution evaporated in a glass dish. Naphthylamine then remains as a malodorous oil of a violet colour. On adding a drop of hydrochloric acid a semi-solid mass of the hydrochloride is formed ; this, after evaporating off the excess of acid, gives a clear solution in water. The solution yields with ferric chloride a bulky blue precipitate which when filtered off, assumes a reddish-purple colour, whilst the filtrate shows a fine violet tint.

XX. WATER-SOLUBLE SUBSTANCES.

Glue occasionally finds its way into mineral oils from carelessly glued casks. It is detected as follows :—100 g. of the oil are thoroughly shaken up with boiling water in a conical flask, the aqueous layer separated off and an aliquot part, say 60 c.c., filtered into a measuring cylinder, and evaporated to dryness in a glass dish on the water-bath. If there is an appreciable residue which, whilst hot, seems to smell of glue, it is extracted two or three times with 5-8 c.c. of hot absolute alcohol, whereby any soap, if present, is removed. The dried residue may be weighed. If it consists mainly of glue, the characteristic smell given off on heating, as also the precipitate obtained from its aqueous solution by tannic acid, serve as confirmatory tests.

Sodium sulphate, to which (a rarely-occurring) opacity or the breaking of mineral oils may be due, is detected in an aqueous extract by means of barium chloride.

XXI. SUSPENDED MATTER.

Mechanical Impurities are detected in pale oils by mere inspection.

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[1] *Chem. News*, 1894, **68**, 297 ; *J. Soc. Chem. Ind.*, 1894, **13**, 69.

For their quantitative determination, 5-10 g. of the sample are dissolved in 100 c.c. of petroleum spirit, or in the case of dark oils in benzene. After standing overnight the solution is poured through a tared filter, and the residue washed thoroughly with the same solvent. The filter is then dried at 105° and weighed.

Bituminous and Pitch-like Matter in suspension in dark oils, beside mechanical impurities, is determined as described in the section on " Mineral Oils," p. 10.

Vaseline, Paraffin, Iron-soap, etc.—These may be detected in the residue after filtration by methods varying with the character of the sample. Iron-soap, which is a not uncommon impurity, is easily recognised by the formation of ferric oxide on ignition.

XXII. ASPHALT AND PARAFFIN IN SOLUTION.

The determination of asphaltic substances and paraffin wax, which must be considered as normal constituents of lubricating oils, is carried out by the methods described under " Crude Petroleum " in the section on " Mineral Oils," p. 9.

XXIII. CHANGES LUBRICATING OILS UNDERGO IN USE.

Recovered Oils.—For reasons of economy, used lubricating oils are collected and again used after some process of purification, whereby mechanical impurities and moisture are removed. In the laboratory water is removed by prolonged warming in a salt-bath, or by adding calcium chloride.

The recovered oils are, as a rule, darker than the original oils. Recovered cylinder oils, containing fatty oils, usually show a notable amount of free fatty acid, asphaltic substances, and of iron-soap; the last-named impurity causes a slight increase of specific gravity and viscosity.

Solid residues found in slide valves, etc.,[1] are extracted first exhaustively with chloroform. The insoluble residue is treated with hydrochloric acid, which decomposes iron-soaps and dissolves iron oxide. The substances insoluble in the acid consist generally of carbon, sand, etc.; of these the carbon is determined by incineration. The portion dissolved by chloroform is treated with petroleum spirit; the insoluble portion is generally identical with the original lubricating oil in specific gravity and elementary composition. The portion insoluble in petroleum spirit is usually soluble in benzene, and consists of asphaltic substances.

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[1] *Cf.* G. Worrall and J. E. Southcombe, *J. Soc. Chem. Ind.*, 1908, **27**, 308 ; J. E. Southcombe, *Ibid.*, 1911, **30**, 261.

Condenser Water being frequently used as feed water for the boilers, the removal of the emulsified oil by some process of purification is imperative. ·To test the efficiency of the purifying plant the oil content in the water, after filtering, is determined by extracting 1-2 litres of the water exhaustively in a separating funnel with freshly distilled ether. The extracts are filtered through a filter paper, the ether distilled off, and the residue dried for ten minutes at 105° and weighed. In view of the small quantities obtained, all sources of error must be guarded against.

E. Graefe recommends the precipitation of the oil in the water by means of alumina or ferric hydroxide, and the extraction of the oil from the precipitate.

B. FATTY OILS.

Since mineral oils have been introduced the use of pure fatty oils as lubricants has been greatly restricted. Nevertheless, considerable quantities are still used, either as such or in admixture with mineral oils.

The suitability of a fatty oil for lubricating purposes is gauged by the purity of the oil, which is ascertained by the methods given in the following Section on " Oils, Fats, and Waxes."

C. MIXTURES OF MINERAL AND FATTY OILS.

Mixtures are dealt with, in the main, by the methods described in the previous section on " Mineral Oils." When it is desired to separate the fatty and mineral oil constituents quantitatively, the procedure given on p. 89 is followed.

D. VASELINE.

Two kinds of vaseline are known in commerce. The one is prepared from crude American petroleum by slow distillation of the volatile fractions and purification of the residue by means of acid or Fuller's earth (Chesebrough vaseline). The other is compounded by dissolving paraffin wax and ceresin in colourless petroleum oils (artificial vaseline, German vaseline). Though used principally for cosmetic and pharmaceutical purposes, vaseline is also, to some extent, applied as a lubricant and as a rust preventative. The laboratory methods for testing vaseline do not differ from those which hold good for petroleum derivatives generally. The specific gravity is best measured at 100° by means of a hydrostatic balance, the thermometer plummet of which has a range reaching to 100°; or, it may be determined with a Sprengel pyknometer. Chesebrough vaseline is stated to have a sp. gr. of 0·845, artificial vaseline of 0·827, both at 100°.

Distinction between Natural and Artificial Vaseline.[1]—A comparison of the viscosities gave the following values :—

Material.	Viscosity (Engler).			
	45°.	50°.	80°.	100°.
Natural American vaseline .	4·8	3·7	2·1	1·6
Artificial vaseline .	does not flow	does not flow	1·5	1·2

Artificial vaseline did not flow in the Engler apparatus even at 65°, whereas when completely molten at 80°, and 100°, it is much more fluid than natural vaseline.

Differences are also observed in the absorption of oxygen. Engler and Böhm heated quantities of 11-15 g. of vaseline with the addition of 2-3 c.c. of water in sealed tubes, with 53-76 c.c. of oxygen for twenty-four hours at 110°-115°, with the following results :—

Material.	Absorption of oxygen.	Quantity of $N/10$ alkali required to neutralise the acid from 100 g. of vaseline.
Natural vaseline . . .	35·0 to 46·5 c.c.	5·5 to 10·5 mg. KOH
Artificial vaseline . .	4·2 ,, 4·7 ,,	0·7 ,, 1·4 ,,
Hog's lard . . .	42·0 ,, 50·0 ,,	31·0 ,, 39·0 ,,

E. SOLID LUBRICANTS.

The substances included under this head vary widely in their nature and composition. General methods of examination, therefore, cannot well be laid down, and it is necessary to modify the laboratory tests according to the nature of the products concerned. Some data as to the composition of solid lubricants have been given above (p. 59). Some varieties melt at 60°-65°, whilst others do not become liquid until temperatures well over 100° are reached.

The following are the main features to be taken into account with regard to solid lubricants :—

    I. *Appearance, etc.*

    II. *Liquefying and Dropping points.*

    III. *Qualitative Composition.*

    IV. *Quantitative determination of :—*

        (*a*) Free Fatty Acid. (*b*) Soap. (*c*) Neutral Fats (glycerides) and unsaponifiable matter (Mineral Oil, Rosin Oil, Wool Grease, etc.). (*d*) Water. (*e*) Glycerol. (*f*) Nitrobenzene and Nitronaphthalene. (*g*) Free Lime. (*h*) Impurities and adulterants.

[1] *Cf.* Engler and Böhm, *Dingl. polyt. J.*, 1886, **262**, 468.

I. Appearance, etc.

A good deal of information as to quality may be gained by inspection. Properly compounded greases should be quite uniform with respect to colour and consistency. Additions of rosin oil, tar oil, nitrobenzene, etc., may be detected by the smell.

II. Liquefying and Dropping Points.

The temperature at which lubricating greases become fluid ranks as one of the most important criteria in their commercial valuation.

These greases do not possess a definite melting point. When warmed, they at first gradually soften at the surface; when further heated, the soap may remain suspended in the molten fatty matter, and complete melting may only occur when a portion of the moisture has been lost by evaporation.

The most serviceable method for the determination of the liquefying and dropping points is that of L. Ubbelohde, in which the temperature is ascertained at which a drop of the sample detaches itself by its own weight from the uniformly heated mass.[1]

The apparatus (Fig. 32) consists essentially of a thermometer a, to which is closely fitted a metal cylinder b, and a small glass receptacle e, 10 mm. long, and having an opening of 3 mm. bore. The metal cylinder has a small opening at c, and grips both the thermometer and the receptacle firmly.

To carry out the test the substance under examination is pressed into the receptacle, and the excess struck off neatly with a knife; the receptacle is then fitted to the thermometer, as shown. In the case of paraffin wax and ceresin, the substance is first melted (with a glass plate held under the receptacle) and the thermometer inserted before it has solidified. Three small guides d prevent the thermometer from being pushed down too far. The thermometer is fixed by means of a cork in a test tube of 4 cm. bore, which is placed in a water-bath (a 3 litre beaker filled with water) and heated slowly so that the temperature rise per minute does not exceed 1°.

Fig. 32.

The temperature at which a drop of the melted lubricant begins to make its appearance is noted as the "Liquefying point," and that at

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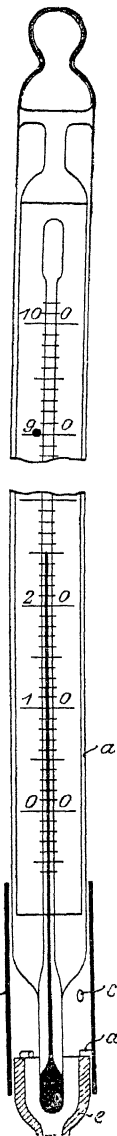
[1] *Z. angew. Chem.*, 1905, **18**, 1220; *J. Soc. Chem. Ind.*, 1905, **24**, 941. The apparatus is supplied by Messrs Bleckmann and Burger, Berlin.

which the first drop falls as the "Dropping point." The latter point is, as a rule, from 3°-6° above the liquefying point, although in some cases the difference may amount to 15° and even more.

III. Qualitative Examination.

If the lubricant should be completely soluble in petroleum spirit or ether, and leave no ash on incineration, it is only necessary to test for rosin and possibly for ceresin, as described on pp. 84 and 187.

The presence of water is indicated by the spurting that occurs on incineration.

The examination of the fatty matter is carried out by the methods described in the following Section (pp. 114 *et seq.*).

As the majority of lubricating greases contain soap, and are therefore only partially soluble in petroleum spirit, the sample is treated with a hot mixture of 9 vols. of petroleum spirit, and 1 vol. of absolute alcohol and, after standing for a short time, filtered whilst still warm. Any insoluble residue (lime, calcium carbonate, barytes, infusorial earth, graphite, etc.) remains on the filter and is examined by the ordinary methods of inorganic analysis.

IV. Quantitative Determinations.

(*a*) **Free Acid.**—Free mineral acid, if present, is detected and estimated by titrating a hot-water extract of the grease. Free fatty acids are determined by the method described in the following Section (p. 130).

(*b*) **Soap.**—For this estimation 10 g. of the sample are dissolved in petroleum spirit, decomposed with hot, dilute hydrochloric acid, and the acid layer of liquid separated. This layer is sometimes coloured red owing to the presence of colouring matters that have been added to the lubricant; in such cases the extraction with hydrochloric acid is repeated until a final colourless extract is obtained. If the sample is not coloured, two successive extractions are sufficient. After the separation of the acid, the residual petroleum spirit is washed either with water or with a solution of sodium sulphate (to avoid the formation of an emulsion), and titrated, after the addition of 20 c.c. of absolute alcohol, phenolphthalein being employed as the indicator.

The acid value obtained represents the sum of the free fatty acids present (ascertained as in (*a*), above) and of the fatty acids formed by the decomposition of the contained soap; the difference represents the fatty acids present as soap. This value may be calculated either to sodium or to calcium soap, as the case may be. It is sufficiently

accurate to take 280 as the mean molecular weight of the fatty acids; should there be reason to assume the presence of rape oil, the mean molecular weight 310 may be adopted.

(*c*) **Neutral Fats (Glycerides) and Unsaponifiable Matter.**—The petroleum spirit solution obtained under (*b*) is freed from fatty acids in the usual manner by extraction with 50 per cent. alcohol, distilled to dryness, and the residue, consisting of neutral fats and hydrocarbons, is weighed. The proportion of glycerides in it is determined by estimating its saponification value (p. 114) and calculating to percentage of the original material.

If the nature of the unsaponifiable matter is to be examined, this constituent is separated from the soap as described above.

(*d*) **Water.**—For most purposes it is sufficiently accurate to mix a weighed quantity of the grease with dried sand, and dry in a water oven.

A more lengthy but more accurate method is that proposed by J. Marcusson, which is carried out as follows:—100 g. of the sample are dissolved in 100 c.c. of xylene in a 600 c.c. Erlenmeyer flask, some fragments of pumice added, and the solution distilled from an oil-bath through a Liebig's condenser. Unless very little water is present, distillation begins below 100°. The distillate is collected in a 100 c.c. measuring cylinder, in which the separation into layers of water and xylene rapidly takes place. Distillation is continued until pure xylene comes over; any drops of water which adhere to the condenser are rinsed down with xylene. The amount of water driven over is read off directly and calculated to percentages of the original substance.

(*e*) **Glycerol.**—The small quantities of glycerol (from 0.5-2 per cent.) occurring in lubricating greases are derived from the saponification of the fatty constituents. The determination of glycerol is carried out only in exceptional cases; the method described in the following Section is then employed (p. 123).

(*f*) **Nitronaphthalene and Nitrobenzene.**—The method for the estimation of these substances has been described above (p. 94).

(*g*) **Free Lime** is determined by heating 10 g. of the sample with 50 c.c. of benzene and 5 c.c. of alcohol for a quarter of an hour under a reflux condenser. The residue is filtered off, thoroughly washed with a hot mixture of benzene and alcohol in the above proportions, and the contained free lime determined by the usual methods.

(*h*) **Impurities and Adulterants.**—Plaster of Paris, barytes, starch, talc, graphite, lampblack, and the like remain undissolved when the sample is extracted with the mixture of benzene and alcohol as described under (*g*), and are determined in the residue thus obtained.

F. WATER-SOLUBLE LUBRICANTS.

Water-soluble lubricants have the property of forming permanent emulsions or almost clear solutions with water. Latterly they have become important articles of commerce, and are prepared by dissolving ammonia-, potash-, or soda-soaps of oleic, sulpho-fatty, rosin, or naphthenic acids in mineral oils. Frequently ammoniacal liquor, petroleum naphtha, or alcohol is added; in some cases the rosin oils are first blown with air. The resulting water-soluble products may be regarded as (colloidal) solutions of mineral oil in an acid soap solution Such preparations are largely employed as lubricants in boring, milling, lathe-cutting, and polishing operations. They have the advantage over aqueous solutions of soap that iron-work with which they come in contact does not rust so easily; other applications are dressing wool-fibre in spinning and weaving, for laying dust in streets, and so on.

The Solidifying Point of such oils is, of course, lowered by the addition of water. Thus a mixture of 80 parts of water with 20 parts of oil is still liquid at $-5°$; for this reason water-soluble oils are often used in place of glycerine in hydraulic presses and pressure mains.

The Emulsifying Properties or Solubility in Water is determined by preparing solutions of varying concentration, and observing the permanence of the emulsion after standing for one or more days. In the case of oils containing ammonia-soaps, the soaps gradually lose ammonia, and the emulsifying properties then fall. Such oils must therefore be tested (and kept) in well-closed receptacles.

Analytical Examination.

This comprises the following determinations:—

(a) Volatile Matter (Water, Alcohol, Naphtha).—The content of water is determined by distilling about 20 g. of the oil in a 1-litre Erlenmeyer flask, with the addition of 100 c.c. of xylene and small pieces of pumice (*cf.*, The determination of water in petroleum in the section on "Mineral Oils," this Vol., p. 5).

The aqueous distillate is fractionated and tested for alcohol, either by the specific gravity of the distillate, or, if necessary, by the iodoform test. To determine the petroleum naphtha, the oil is decomposed by dilute sulphuric acid, and the volume of naphtha either measured directly or after being distilled over by steam.

If both alcohol and naphtha are present, the oil is distilled with acid potassium sulphate, and the distillate shaken with sodium hydroxide, whereby the alcohol is completely separated. The volume of naphtha

is then measured, and the alcohol separated from the alkaline liquid by a further distillation, and determined as above.

(*b*) **Free Organic Acid.**—In the absence of ammonia the sample is titrated with $N/10$ alcoholic sodium hydroxide.

In the presence of ammonia-soaps, it is necessary to determine the ammonia by distilling 20-30 g. of the sample with an excess of concentrated sodium hydroxide solution from a very capacious conical flask fitted with a vapour-trap; the distillate is collected in $N/10$ sulphuric acid, and the excess titrated back with standard alkali.

Should ammonia be the only base present, it may be determined by simply titrating an aqueous emulsion of the material with $N/2$ hydrochloric acid, using methyl orange as the indicator. The amount of acid corresponding to ammonia, found by either method, is calculated to "acid value," and is subtracted from the total acid value obtained by direct titration; the difference represents free acid.

(*c*) **Neutral Fatty Matter.**—The sample is shaken up with petroleum spirit and $N/10$ alcoholic sodium hydroxide (50 per cent. alcohol), and the neutral fat isolated as described above (p. 89).

(*d*) **Soap.**—1. When the soap acids present are ordinary fatty or naphthenic acids, sulphonated fatty acids or oxidised resin acids being absent, the soap content of the material can be determined as in ordinary lubricants (p. 88). Ammonia, if present, beside fixed alkali, must be determined and allowed for.

2. Sulphonated acids or oxidised resin acids introduce complications, as they combine with considerably more alkali than ordinary fatty acids. Thus sulphonated fatty acids require one equivalent of alkali for the carboxyl group and a second one for the sulphonic acid group. In such cases the organic acid present in the form of soap is determined as above, and in addition the total alkali absorbed is determined gravimetrically by incineration. The carbonate found by incineration is calculated to metal and added to the soap acid, whereby the amount of soap as such is arrived at.

Example :—

Free acid found $= 10$ ("Acid Value").

Weight of total acid, as under $c = 15$ g. (corresponding to "acid value" 30).

Hence, weight of free acid $= \dfrac{15 \times 10}{30} = 5$ g. and

weight of soap acid $= 10$ g.

Alkali found as ash, calculated to metal, $= 2$ g.

Hence weight of soap present approximately $= 10 + 2 = 12$ g.

Whether soap alkali is to be determined by titration (1) or by incineration (2) is decided by a preliminary qualitative test of the isolated organic acids.

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OILS, FATS, AND WAXES

By the late J. Lewkowitsch, M.A., Ph.D.   English translation
revised by the Author.

CLASSIFICATION OF OILS, FATS, AND WAXES.

The oils, fats, and waxes which form the raw material of the fat and oil industries are found ready formed in plants and animals. The oils and fats differ chemically from the waxes, in that the former are glyceryl esters of fatty acids, whereas the latter are esters derived from fatty acids and monohydric alcohols. On this basis it is easy to distinguish between oils and fats, on the one hand, and waxes, on the other hand, by chemical means; namely, by the detection of glycerol. In nature apparently only triglycerides occur; mono- and diglycerides are the result of a secondary reaction which may be regarded as a natural hydrolysis. The present section deals only with the triglycerides. The natural oils and fats represent complicated mixtures of the most varied triglycerides, including not only simple triglycerides containing a single fatty acid, but also mixed triglycerides in which the glyceryl radicle is combined with different fatty acids; hence an exhaustive scheme of analysis similar to the systems of inorganic analysis is impracticable. There is, however, no necessity for such a scheme, as it is generally possible to indentify a given oil, fat, or wax on the basis of a systematic method of examination, and in addition to determine whether a sample is pure or adulterated; these are the most important problems in their technical analysis.

It is also possible, with the help of the methods described below, to identify a mixture of two or more oils or fats, and to obtain an approximate indication as to their relative proportions. The larger the number of components in a mixture, the more difficult their detection and estimation will naturally be. If, however, the tests are applied on a strictly logical basis, and the methods described are combined in a suitable manner, it is frequently possible to ascertain, with sufficient accuracy for technical purposes, the composition of mixtures which appear at first to be hopelessly complicated.

As glycerol is obtained as a product of saponification from all oils and fats, the differentiation of the glycerides must necessarily depend upon the differences of the several fatty acids occurring in the natural

oils and fats, disregarding for the present the more intricate and hitherto scarcely investigated differences depending upon the isomerism of the mixed glycerides. Hence it follows that in addition to the examination of the oils and fats themselves, an investigation of the fatty acids is of great importance.

In the case of the waxes, whose alcoholic constituents, in contra-distinction to glycerol, are insoluble in water, the examination of the alcohols is of increased importance. The alcoholic compound is spoken of in technical practice as " unsaponifiable matter," although this expression, in contrast to saponifiable matter, includes not only the alcohols, but also (unsaponifiable) hydrocarbons, such as, mineral oils, rosin oils, tar oils, etc. Strictly speaking, only the fatty acids themselves are saponifiable, that is, capable of conversion into soaps. As, however, glycerol, in itself unsaponifiable, is soluble in water, in contradistinction to the alcohols of the waxes and to the hydrocarbons, the glycerides are technically considered as completely saponifiable.

A systematic investigation would therefore comprise the examination of the oils, fats, and waxes of the fatty acids, and of the unsaponifiable matter.

THE EXAMINATION OF OILS, FATS, AND WAXES.

Both physical and chemical methods are employed in the examination of natural oils and fats.

A.—PHYSICAL METHODS.

Preliminary indications are obtained from the colour, consistency, and also from the smell and taste. The colour is chiefly of importance for the recognition of certain individual substances amongst the solid fats, e g., raw palm oil and aouara oil. The consistency at ordinary tempera-ture helps to give a ready indication as to whether a sample belongs to the class of liquid fats (oils) or of solid fats. Smell and taste characterise the oils derived from marine animals. In the case of other commercial oils and fats these " organoliptic " indications can only be made use of by experts, for they require an extensive experience which is not at the disposal of every technical chemist, the acquirement of which is, however, very desirable. In the examination of oils and fats which form articles of food, both the smell and taste are of very great importance.

The determination of the specific gravity, melting point, solidifying point (especially of fatty acids), and of the refractive index is of primary importance. The viscosity, the optical rotation, and the solubility are frequently determined as subsidiary tests.

I. DETERMINATION OF THE SPECIFIC GRAVITY.

The specific gravity of liquid oils and waxes is determined by the hydrometer, pyknometer, or the hydrostatic balance. It is advisable to make the determinations at the normal temperature of 15° C. (or, as is usual in England and America, at 15°·5 C., corresponding to 60° F.), as most of the observations recorded in the literature have been made at this temperature, and can therefore be used for purposes of comparison. However, if it is impossible to make the determination at this temperature, a correction of ±0·00064 per degree is applied. The determination is often made at higher temperatures. In such cases, Sprengel's pyknometer (Fig. 33) is used. The Sprengel tube is filled with the fat by dipping the tube b into the oil and sucking it up with the aid of a rubber tube attached to a. The tube is then suspended as deeply as possible in a beaker of water, which is heated to boiling. The oil expands in the Sprengel tube in the direction of least resistance towards a, so that the side tube a always remains full. If the meniscus of the liquid lies beyond m, the excess is removed at a by a small roll of filter paper. If, on the other hand, there is too little oil in the tube, a drop of the oil is brought in contact with a on a glass rod, and is drawn into the tube by capillarity. The specific gravity of the substance is compared with that of water at the same temperature as found by determining the specific gravity of water under identical conditions. The temperature of the water in the control test must always be stated.
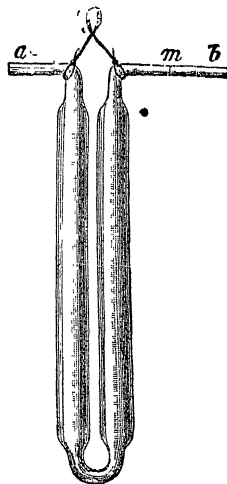
FIG. 33.

The specific gravity of solid fats is usually determined at 100°, in the same manner as described above. In the case of beeswax, however, the test is generally carried out as follows:—The wax is first melted on a watch-glass on the water-bath and allowed to solidify gradually. Small pieces are then cut out of the mass, brushed with a damp brush to remove air bubbles, and carefully introduced into dilute alcohol with the aid of a pair of forceps. Water or alcohol, as the case may be, is then added until the wax neither floats nor sinks, but remains suspended in the liquid. The alcohol is filtered off, and its specific gravity determined; the value obtained is, of course, identical with the specific gravity of the wax.

As a rule the determination of the specific gravity gives but little information as to the nature of a given sample. It furnishes, however, indications in the case of the liquid waxes, which are characterised by a

low specific gravity, as also in the case of castor oil, the specific gravity of which is high. The specific gravity also frequently helps to indicate adulteration, or serves as a confirmation of conclusions drawn from the other methods detailed below. A list of the specific gravities of the commoner oils, fats, and waxes is given below (see Tables, pp. 146 *et seq.*).

II. DETERMINATION OF THE MELTING POINT AND THE SOLIDIFYING POINT.

The fats and waxes have no sharply defined melting points, such as pure chemical substances exhibit when tested in capillary tubes. If this method be applied to fats, the melting point extends over several degrees, the substance first softening, then melting at the edges and becoming translucent, and finally melting to a clear liquid. Hence there is considerable uncertainty as to what temperature should be accepted as the melting point. Some chemists define the melting point as that temperature at which the fat softens so that it is driven up the tube by the hydrostatic pressure of the water, when immersed in water in a small tube open at both ends. Others, again, dip the bulb of a mercury thermometer into the molten fat, allow it to solidify, and take that temperature at which the fat softens sufficiently to drop off the bulb as the melting point. As several different methods are still in technical use, it is absolutely essential to state precisely in every instance the procedure by which the melting point has been determined.

Further, it is to be noted that a freshly melted sample does not show the correct melting point, and that it is necessary to allow such a sample to remain at rest for twenty-four hours before determining the melting point.

The following methods are still in commercial use in tendering for supplies of fats :—

Pohl's method, which consists in dipping the bulb of a thermometer into the molten substance so that a thin layer remains on the glass. The thermometer is then allowed to stand for one to two days in a wide test tube, which is corked so that the bulb of the thermometer is at a distance of 1·25 cm. from the bottom. The test tube is then heated in a water-bath, and the temperature at which the fat collects as a drop at the bottom of the bulb is taken as the melting point.[1] L. Ubbelohde has increased the accuracy of the method by the introduction of a special thermometer (see " Lubricants," Fig. 32, p. 99), to the bottom of which a small glass vessel containing a hole is attached. The temperature at which the fat softens may be recognised by the formation of a drop, and the melting point is taken as the temperature at which it drops off.

[1] *Cf.* R. Meldrum, *Chem. News*, 1913, **108**, 199, 233.

Hitherto this method has not met with general acceptance, at any rate in this country, and the somewhat high cost of the apparatus forms a drawback to its introduction.

A better method is that introduced by Boverton Redwood, which gives good results with sufficiently solid fats, when applied in the following manner :—A lump of the fat, *not recently melted*, is brought on to a. bright surface of mercury, and slowly warmed in a dish over a beaker. The temperature at which the fat spreads over the mercury is taken as the melting point.

• The determination of the melting point is still frequently made in a capillary tube. As the fat passes through successive phases of softening, translucency, and finally of melting, it is usual to state the initial and final point of the melting.   •

The determination of the melting point is only of importance in the case of "winter oils" and chocolate fats.

The solidifying point of the fatty acids, or, as it is technically called, the "titre," is of far greater importance. For this purpose the fatty acids must first be isolated by the method described in the following Section (p. 174).

III. DETERMINATION OF THE REFRACTIVE INDEX.

The determination of the refractive index, which has been very considerably simplified by the introduction of the oleo-refractometer of Amagat and Jean, and especially by the construction of Zeiss' butyro-refractometer, forms one of the simplest and most important preliminary tests for oils and fats, especially of butter fat and of lard. Formerly unjustified objections were raised by various workers against the reliability of the refractometric method; more recently, however, on account of the ease and rapidity of measurement by the butyro-refractometer, this mistrust has given place to undue optimism, as is evidenced by many recent publications, so that a warning in this connection is necessary. In the testing of butter fat especially, conclusions have been drawn which are unsubstantiated. With the help of the butyro-refractometer it is possible to tell at a glance whether a butter fat has been grossly adulterated ; but when the readings differ but slightly from the "normal" value, or even when "normal figures" are obtained, this is no proof of the purity of a butter fat, for it is an easy matter to prepare mixtures of margarine and cocoa-nut oil, which give the same refractive index as does normal butter fat. Even when abnormal values are obtained, this does not afford certain proof of adulteration, for there are certain kinds of butter which give refractometric figures deviating considerably from the normal ones. The refractometric test must, therefore, be considered only as a

preliminary test, although one of great importance. It would be quite unjustifiable to attempt to identify oils and fats by this method alone.

As a rule, there exists a certain correlation between the refractive index and the iodine value, as may be gathered from the Tables given on pp. 146 *et seq.*, in which the refractive indices of the most important oils and fats are collated.

The Butyro-Refractometer.

The essential parts of this instrument (Fig. 34) aré two glass prisms
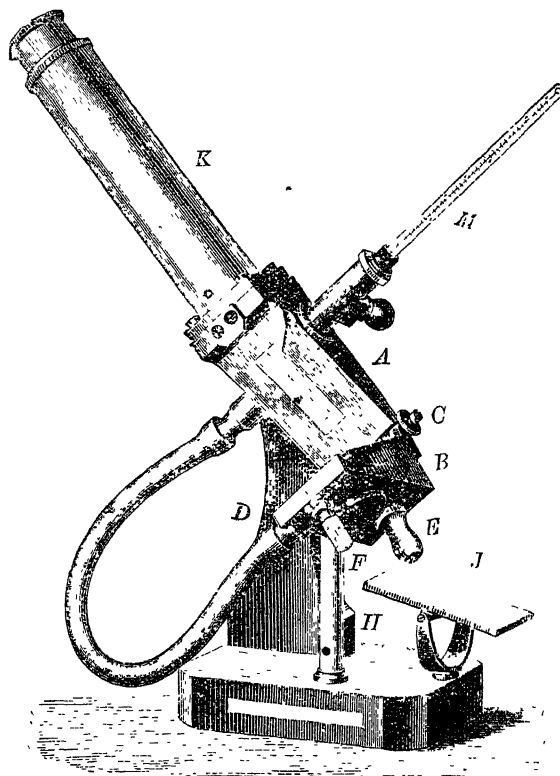
Fig. 34.

contained in the two metal cases A and B. One face of each of the prisms is exposed. The case B can be rotated on the axis C, so that the two exposed faces of the prisms can be brought into contact and removed from one another. The two metal cases are hollow; if warm water is allowed to flow through them, the glass prisms are heated. A metal jacket which holds a thermometer M is attached to the inner case, the mercury bulb reaching into the case. K is a telescope

containing a scale divided from 1-100, and J a mirror for illuminating the prisms and scale.

The heating arrangement shown in Fig. 35 is used to warm the water. The boiler, heated by the gas burner B_1, is fitted with a thermometer T_1 and a thermo-regulator S_1. The neck A_1 is connected by a glass and rubber tube with a vessel C_1, placed above the heater and charged with cold water; the rubber tube carries a screw clip E_1. Before heating the boiler, water is allowed to flow into it by opening the clip E_1. The clip is then closed, and the rubber tube G_1 is connected to the gas supply and the flame lit at B_1. By turning the screw P_1, the flow of gas to the burner B_1 is regulated once for all, so that a constant temperature of the water in the boiler is maintained.

Directions for fitting up the Refractometer in connection with the Heating Apparatus.— The instrument is placed in a convenient position, and is illuminated either by daylight or by lamplight.

The rubber tube attached to the prism jacket of the refractometer (Fig. 34) is connected to the nozzle D_1 of the heating bath; at the same time a rubber tube is attached to the outlet of the metal jacket of the refractometer and is led to an empty vessel placed at a lower level, or to a sink. The screw clip E_1 is then opened, and water is allowed to flow from the vessel C_1 (Fig. 35) into the heating bath. This causes warm water to flow through the outlet tube of the bath and so through the rubber tube D into the prism jacket B, thence through the rubber tube shown in Fig. 34 into the other prism jacket, through the metal jacket of the thermometer, and so through the outlet and rubber tube. The two glass prisms and the bulb of the thermometer are thus heated by the warm water.

FIG. 35.

The flow of water through the heater is regulated by the screw clip, so that the water trickles out in a slow stream, and the thermometer indicates the desired temperature (as a rule, 40°).

Application of the Oil or Fat to the surface of the Prism, and Reading of the Refractometer Value.—The prism jacket of the refractometer is opened by turning the milled head F (Fig. 34) about half a revolution to the right until it releases the catch, whereupon one half of the jacket may be turned round the other. The support H holds B in the position shown in Fig. 34. The instrument is moved by
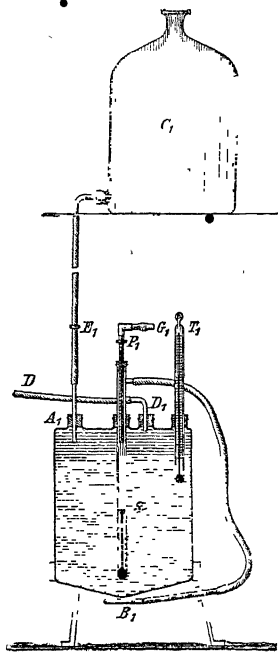
the left hand into such a position that the exposed surface of the prism B is approximately horizontal, and three drops of the filtered oil (or molten fat) are applied to the surface with the aid of a small glass rod, and spread with the rod, so that the whole surface is covered. The prism jacket is then closed by bringing B and A together, and turning the milled head to the left into its original position. The mirror is then brought into such a position that the border line between the bright and the dark portions of the field is seen distinctly. The upper part of the telescope, which can be drawn out, is focussed so that the scale appears quite distinct.

Three minutes are allowed to elapse before reading off the scale division at which the border line between the bright and dark portions of the field lies ; fractions of the marked divisions are estimated by the eye. The thermometer is read immediately after taking the reading.

The refractometer readings, if not taken at 40°, must be corrected to this temperature by adding 0·55 division to the reading for every degree of temperature above 40° ; conversely, for every degree below 40°, 0·55 division must be subtracted.

Cleaning of the Refractometer.—After every experiment, the surfaces of the prisms and their metal fittings must be carefully cleaned with soft linen or soft filter paper, moistened with ether.

Testing the Adjustment of the Refractometer Scale.—The refractometer itself should be tested from time to time with the normal liquid supplied with the apparatus.

For this purpose the thermometer is fitted into position, water at the ordinary temperature allowed to flow through the prism jacket (no heating being necessary in this case), and the refractometer number of the normal liquid determined, the thermometer reading being taken at the same time. If the scale is correctly adjusted, the following refractometer numbers should be obtained at different temperatures :—

Temperature.	Divisions on scale.	Temperature.	Divisions on scale.
25° C.	71·2	16° C.	76·7
24°	71·8	15°	77·3
23°	72·4	14°	77·9
22°	73·0	13°	78·6
21°	73·6	12°	79·2
20°	74·3	11°	79·8
19°	74·9	10°	80·4
18°	75·5	9°	81·0
17°	76·1	8°	81·6

If necessary, the scale must be adjusted with the key supplied with the instrument.

The divisions of the scale correspond to the following refractive indices :—

Divisions on scale.	Refractive index.	Difference.
0	1·4220	0·0080
10	1·4300	0·0077
20	1·4377	0·0075
30	1·4452	0·0072
40	1·4524	0·0069
50	1·4593	0·0066
60	1·4659	0·0064
70	1·4723	0·0060
80	1·4783	0·0057
90	1·4840	0·0055
100	1·4895	

Intermediate values are easily obtained by interpolation.

The refractometers of the newest construction are provided with a micrometer screw, which permits of a more accurate estimation of the tenths of a degree.

IV. THE DETERMINATION OF THE VISCOSITY.

This is determined in one of the known forms of viscometer, the Redwood's viscometer being in general use in England, that of Saybolt in the United States, and that of Engler in Germany.   These apparatus and the method of testing are fully described in the section on " Lubricants," pp. 66 and 68.   This test is of importance only for oils which are used for lubricating purposes, *e.g.*, rape oil and blown oils.

V. DETERMINATION OF THE SOLUBILITY.

This test is of secondary importance, as almost all fats are readily soluble in the common solvents.   Castor oil alone forms an exception, being readily soluble in alcohol and sparingly so in petroleum hydrocarbons.   This abnormal behaviour may be used to identify castor oil, and to distinguish it from other oils.

VI. OPTICAL ROTATION.

This has up to recently been seldom used in technical analysis, and was chiefly applied for the detection of rosin oils in fatty oils.   Recently, however, this test has gained in importance, since the oils of the chaulmoogra group can be identified with the aid of the polariscope. In this manner the poisonous " Cardamom oil " (which the author first identified as chaulmoogra oil) can be recognised in margarines.

B.—CHEMICAL METHODS.

The chief chemical methods which are used in technical analysis consist in the determination of certain values depending upon the nature of the fatty acids contained in the oils, fats, and waxes. As these figures are a measure of the quantity of different fatty acids or groups of fatty acids present, without, however, showing their absolute quantity, these methods are appropriately termed "quantitative reactions."

Besides these quantitative reactions, a number of other tests are available which may conveniently be grouped together as "qualitative methods."

I. QUANTITATIVE METHODS.

The values which are obtained by quantitative methods may be divided into two classes.[1]

(a) *Characteristics*, that is, numbers which determine the nature of an oil, fat, or wax, and may therefore serve for the identification of a given specimen.

(b) *Variables*, that is, numbers which serve to determine the quality of a product, as these numbers depend upon the method of purification of the raw product, the age, rancidity, and other features.

The acetyl value takes up an intermediate position, as it may sometimes be regarded as a characteristic and sometimes as a variable.

(a) Characteristics.

The following characteristics, which are given in the order of their relative importance, will be considered :—

1. Saponification Value.
2. Iodine Value.
3. Reichert (Reichert-Meissl, or Reichert-Wollny) Value.

1. Determination of the Saponification Value.

The saponification value (Köttstorfer Value) indicates the number of milligrams of potassium hydroxide required for the saponification of 1 g. of a fat or wax.

The saponification value is determined as follows :—1·5-2·0 g. of the filtered fat or wax are weighed into a 150-200 c.c. flask (of good glass), and 25 c.c. of an approximately $N/2$ alcoholic solution of potassium hydroxide are added. The alkali is best measured out from a pipette,

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[1] The expression "constant" originally used in the older editions of Lewkowitsch's *Chemical Technology and Analysis of Oils, Fats, and Waxes,* may be advantageously replaced by " characteristics," as the former expression has been taken by many chemists in far too literal a sense.

which is always allowed to run out in exactly the same manner—both in the experiment proper and in the control test. The flask is attached to a reflux condenser or a simple glass tube and heated either on a water-bath, or over a small flame, so that the alcohol simmers gently. The flask is agitated from time to time, as long as any oil layer is visible at the bottom. After half an hour the saponification is almost invariably complete; only in the case of waxes (*cf.* p. 184) is it necessary to use strong alcohol and to boil briskly for at least an hour over a free flame. (The stronger the alcohol used for the preparation of the alcoholic potash, the more quickly the saponification proceeds. It is inadvisable to use alcohol of less than 96 per cent. strength.) 1 c.c. of a 1 per cent. alcoholic solution of phenolphthalein is then added, and the excess of alkali is titrated back with $N/2$ hydrochloric acid.

A blank test is conducted in exactly the same way with 25 c.c. of the alcoholic potassium hydroxide solution. The difference of the amounts of acid used in the two experiments corresponds to the potassium hydroxide that has combined with the fatty acids.

Example.—1·6775 g. of lard were saponified with 25 c.c. of an alcoholic potash solution, which corresponded to 24·6 c.c. of $N/2$ hydrochloric acid (1 c.c. = 0·0561 g. KOH). For the back-titration 12·95 c.c. of $N/2$ hydrochloric acid were required. Hence, the amount of alkali used in combining with the fatty acids is 24·60 − 12·95 = 11·65 c.c.

This corresponds to $\dfrac{11·65 \times 0·0561}{2}$ = 326·78 mg. KOH.

Hence 1 g. of fat requires $\dfrac{326·78}{1·6775}$ = 194·8 mg. KOH.

The saponification value is therefore 194·8.

The "cold saponification" suggested by R. Henriques[1] has no advantage over the above method, except in testing india rubber substitutes.

The saponification values of most oils and fats lie in the neighbourhood of 195, and the mean molecular weight of their fatty acids (*cf.* p. 131) is therefore approximately 276. The oils of the rape oil group are, however, distinguished by a lower saponification value, namely, about 175, as these oils contain considerable quantities of erucic acid of molecular weight 338. On the other hand, oils and fats containing considerable quantities of volatile fatty acids have a higher saponification value than 195. Thus, the saponification value of butter fat is 227. Fats containing much myristin or laurin have still higher numbers; thus the saponification values of the fats of the cocoa-nut oil rise as high as 240-260.

The saponification values of the waxes are far lower than those of

[1] *Z. angew. Chem.*, 1895, **7**, 721 ; 1896, **8**, 221 ; *J. Soc. Chem. Ind.*, 1896, **15**, 299, 476.

the oils and fats, and are for the most part between 80 and 136. It is therefore possible to distinguish between the waxes (liquid and solid), the oils of the rape oil group, butter fat, and the oils of the cocoa-nut oil group by the determination of the saponification value alone. This holds, of course, only on the assumption that the samples under examination contain only negligible amounts of unsaponifiable oils, as the latter obviously reduce the saponification value.

The influence of free fatty acids in a fat on the saponification value has been investigated by the author.[1]

2. Determination of the Iodine Value.

The iodine value indicates the amount of iodine chloride, expressed in per cent. of iodine, which the fat or wax is capable of absorbing. The iodine value is a measure of the unsaturated fatty acids, as these acids, both in the free state and also when combined with glycerol, absorb one molecule of iodine chloride, corresponding to two atoms of iodine, for each pair of doubly linked carbon atoms.

The determination of the iodine value was introduced into fat analysis by A. von Hübl, and is carried out, either in the form originally proposed by him, or as modified by J. Wijs. On the basis of many years' experience, the latter is to be recommended as the more rapid and reliable method. As, however, the Wijs method has not yet met with the general acceptance which it undoubtedly deserves, both methods will be described.

Hübl's Method.—The quantities of oil or fat taken for the test are as follows:—Drying oils and fish oils, 0.15-0.18 g.; semi-drying oils, 0.2-0.3 g.; non-drying oils, 0.3-0.4 g.; solid fats, 0.8-1.0 g. The oil is best weighed in a small weighing bottle, the cork of which is fitted with a small pipette, so that a certain number of drops of the oil or molten fat can be withdrawn with the help of a rubber tube fixed to the pipette. With a little practice the weight can be estimated to within a few centigrams by the number of drops. The weighed quantity is introduced into a well-stoppered flask of 500-800 c.c. capacity, 10 c.c. of carbon tetrachloride (or chloroform) added, and the substance is brought into solution, if necessary, by gentle warming; 25 c.c. of an iodine chloride solution are then introduced by means of a pipette, this solution being prepared as follows:—Two solutions are made up, one of 25 g. of pure iodine in 500 c.c. of 95 per cent. alcohol; and the other of 30 g. of mercuric chloride in the same quantity of alcohol; these solutions are kept separate. The quantity necessary for an experiment is made up twenty-four hours before use by mixing equal volumes of the two solutions. The mixture must not be used at once, as the iodine chloride solution alters its titre rapidly immediately after its prepara-

[1] *Chemical Technology and Analysis of Oils, Fats, and Waxes*, vol. i., p. 385.

tion; the titre alters gradually even after twenty-four hours' standing, but remains sufficiently constant during the experiment.

In order to avoid any loss of iodine by evaporation, it is advisable to moisten the glass stopper of the flask with a concentrated solution of potassium iodide. A clear solution should be obtained on gently agitating the flask; if it is not clear, more carbon tetrachloride (or chloroform) must be added. The flask is then allowed to stand, protected from the light. At the same time a blank experiment is made, in which exactly the same quantity of carbon tetrachloride (or chloroform) and iodine chloride are brought together; this solution serves to determine the titre. After about two hours the solution must still have a deep brown colour, otherwise the quantity of iodine is insufficient, and a further quantity of 25 c.c. of the iodine chloride solution must be added. The absorption of the bulk of the iodine chloride takes place during the first two hours; after this time it becomes more sluggish. It must not, however, be considered as complete before about six to eight hours in the case of solid fats and non-drying oils, or twelve to eighteen hours in the case of drying oils and fish oils. For semi-drying oils eight to ten hours suffice.

After the necessary time has elapsed, 20 c.c. of a 10 per cent. solution of potassium iodide are added, and, after shaking, 400 c.c. of water. If a red precipitate of mercuric iodide separates, more potassium iodide solution must be added. The excess of free iodine is then titrated back by the addition of $N/10$ sodium thiosulphate, the titre of which has been accurately determined with potassium bichromate. The contents of the flask are gently rotated during the titration, so that the free iodine which is dissolved in the carbon tetrachloride (or chloroform) may pass into the aqueous solution. When the colour, which was originally deep brown, has become pale, a few drops of starch solution are added and the titration completed. The iodine in the blank test is determined in exactly the same manner. The difference between the two results corresponds to the quantity of iodine chloride absorbed, and is calculated to per cent. of iodine.

The potassium bichromate solution used for fixing the strength of the thiosulphate solution is made up by dissolving 3.8657 g. of bichromate in 1000 c.c. of water; 1 c.c. of this solution is =0.01 g. I. 10 c.c. of a 10 per cent. potassium iodide solution are placed in a stoppered bottle, 5 c.c. of hydrochloric acid added, 20 c.c. of the bichromate solution then run in from a burette, and the liberated iodine titrated with the thiosulphate solution.

To save time in the calculations, the author has prepared a Table in which the logarithms of the quotients $\dfrac{0.2}{\text{c.c. thiosulphate}}$ are given.[1]

[1] J. Lewkowitsch, *Laboratory Companion to the Fats and Oils Industries*, Table 11, p. 28.

Example.—0·3394 g. of lard were treated with 25 c.c. of iodine chloride, which required in a blank test 60·9 c.c. of thiosulphate solution, 16·45 c.c. of which were equivalent to 0·2 g. of iodine. For titrating back the excess of iodine 39·6 c.c. of thiosulphate solution were required. Hence the iodine absorbed corresponds to 60·9 − 39·6 = 21·3 c.c. thiosulphate solution. Since 16·45 c.c. of thiosulphate are equivalent to

0·2 g. iodine, the iodine absorbed is $\dfrac{0·2 \times 21·3}{16·45} = 0·2589$ g. Hence

100 g. of lard absorb $\dfrac{0·2589 \times 100}{0·3394} = 76·28$ g. iodine.

The iodine value of the sample is therefore 76·28.

For a discussion of the theory of the complicated chemical changes occurring in Hübl's iodine chloride solution, *cf.* Lewkowitsch, *Chemical Technology and Analysis of Oils, Fats, and Waxes*, vol. i., pp. 398 *et seq.*

Wijs' Method.—Solutions of 7·9 g. iodine trichloride and 8·7 g. iodine respectively, in glacial acetic acid, are made up by warming on the water-bath, taking care that no moisture from the air be absorbed. The glacial acetic acid must be pure (it must give no green tinge when warmed with potassium bichromate and concentrated sulphuric acid). The two solutions are poured into a litre flask and made up to 1 litre with glacial acetic acid.

In a laboratory in which many iodine values are determined, it will be found cheaper to dissolve 13 g. of iodine in 1 litre of glacial acetic acid, to ascertain the exact titre of the solution by means of thiosulphate, and then to pass washed and dried chlorine gas into the solution until the titre has exactly doubled. With a little practice, the exact point at which the iodine has just become converted to iodine chloride can be judged by the change in colour of the solution.

The iodine value is determined exactly in the manner described above for Hübl's method. Carbon tetrachloride is used as the solvent instead of chloroform, as the latter frequently contains alcohol. Wijs' solution can, however, be used immediately after preparation, and remains unaltered for months, so that it is not necessary to carry out a blank test in every case. The solution also offers the great advantage that solid fats and non-drying oils require only half an hour, semi-drying oils one hour, and drying oils two to six hours (according to the iodine absorption) for the completion of the reaction.

The iodine value is one of the most important data in the analysis of fats, as all oils, fats, and waxes within the groups given in the Tables below can be arranged in a natural system according to the magnitude of the iodine values (see Tables, pp. 146 *et seq.*).

3. Determination of the Reichert (Reichert-Meissl, or Reichert-Wollny) Value.

The Reichert (Reichert-Meissl, or Reichert-Wollny) value indicates the number of cubic centimetres of $N/10$ potassium hydroxide necessary for the neutralisation of that portion of the soluble volatile fatty acids which is obtained from 2·5 g. (or 5 g.) of a fat by the Reichert distillation process.

E. Reichert, who introduced this method into the analysis of fats, used 2·5 g. of fat for the estimation; it is, however, now more usual to take 5 g. of fat, as recommended by E. Meissl and R. Wollny. The Reichert-Meissl or Reichert-Wollny value is not, however, simply twice that of the Reichert value, as is frequently assumed. It is always necessary to state precisely how the distillation has been carried out,
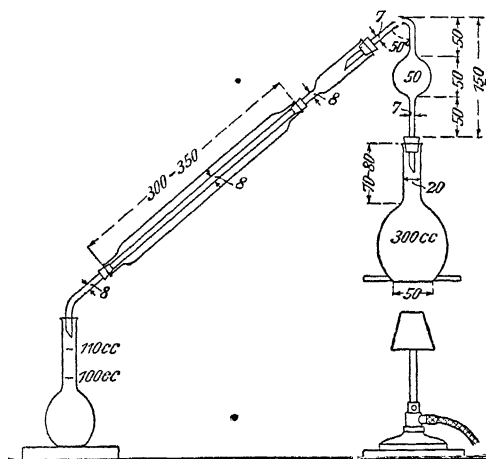
FIG. 36.

as the results differ somewhat according to the method adopted. As a rule, however, the Reichert-Meissl or Reichert-Wollny value may be taken as approximately 2·2 times the Reichert value.

The following details of the method have been agreed upon by a Committee of the Government Laboratory and the Society of Public Analysts.[1]

The Reichert-Wollny Method.—The apparatus used is shown in Fig. 36. The fat is filtered and 5 g. are introduced into a 300 c.c. flask. A sodium hydroxide solution is made up by dissolving pure 98 per cent. sodium hydroxide in an equal quantity of water. This solution must be preserved from the action of atmospheric carbon dioxide as completely as possible. 2 c.c. of this solution and 10 c.c. of alcohol (about 92 per cent. strength) are added to the fat, and the mixture is

[1] *Analyst*, 1900, 25, 309.

heated under a reflux condenser for about fifteen minutes on a boiling water-bath. The alcohol is then distilled off on the water-bath until a dry soap is left. This is dissolved in 100 c.c. of hot water, which has been previously boiled for at least ten minutes, the flask being heated until all has passed into solution. Then 40 c.c. of $N/1$ sulphuric acid, and three or four pieces of pumice, about the size of peas, are added, and the flask at once connected by means of the bulb-tube to the condenser. The flask is heated on a sheet of asbestos 12 cm. in diameter, and having a hole in its centre 5 cm. in diameter. The flame is at first turned low to melt the fatty acids. When these have become clear, the flame is turned up, and the solution distilled so that exactly 110 c.c. pass into the measuring flask in thirty (twenty-eight to thirty-two) minutes. The distillate is shaken, 100 c.c. are filtered off, 0·5 c.c. of an alcoholic solution of phenolphthalein (1 g. in 100 c.c.) added to the filtrate, and this then titrated with $N/10$ alkali or baryta.

A blank experiment is made in exactly the same manner with the same reagents. The $N/10$ alkali used in this test must not exceed 0·3 c.c. The amount of alkali used in the blank experiment is subtracted from that used in the actual experiment, and the difference is multiplied by 1·1.

The number thus found is the Reichert-Wollny value; the Reichert-Meissl value is almost identical with this. The Reichert-Meissl value of the majority of oils and fats, namely, those whose saponification value is below 200, is less than 0·5. All oils and fats whose saponification values exceed 200 have Reichert-Wollny values above 1·0.

The Reichert-Meissl value furnishes important information as to the nature of an oil or fat. Thus, butter fat is characterised by a Reichert-Wollny value of about 27-29, the fats of the cocoa-nut oil group have a Reichert-Wollny value of 5-8, and finally, dolphin oil and porpoise oil have Reichert-Meissl values of 47-120 (cf. Tables on pp. 146 et seq.).

The Leffmann-Beam saponification method is generally used when it is desired to determine at the same time the titration number of the insoluble volatile fatty acids (see p. 156).

A solution of 100 g. of sodium hydroxide in 100 c.c. of water is made up, and 20 c.c. of this solution are mixed with 180 c.c. of pure concentrated glycerol. 20 c.c. of this glycerol alkali solution and 5 g. of the filtered fat are placed in an Erlenmeyer flask, and heated for two or three minutes over a free flame until the water is driven off, and the liquid is clear. For the rest, the procedure is the same as described above.

Determination of the Acetyl Value.

The acetyl value indicates the number of milligrams of potassium hydroxide required for the neutralisation of the acetic acid obtained on saponifying 1 g. of the acetylated fat or wax.

The determination of the acetyl value of oils and fats is based on the principle that glycerides containing hydroxylated fatty acids take up an acetyl group for each hydroxyl group on heating with acetic anhydride. The chemical change consists, therefore, in the replacement of the hydrogen atom of the alcoholic hydroxyl group or groups by the radicle of acetic acid.

The determination of the acetyl value is carried out by the method given by the author[1] as follows :—10 g. of oil are heated for one or two hours under a reflux condenser with double the quantity of acetic anhydride. The solution is then poured into a beaker of 1000 c.c. capacity, mixed with 500-600 c.c. of boiling water, and heated for half an hour, a slow current of carbon dioxide being at the same time passed through the liquid ; this prevents the liquid from bumping. The mixture is allowed to separate into two layers, the water layer syphoned off, and the oily layer boiled out three times successively with water. The last traces of acetic acid are removed in this way, the liquid being tested with litmus paper. If the heating be unduly prolonged, the acetyl derivative is hydrolysed to an appreciable extent, and the acetyl value found is too low. The acetylated product is then filtered through a dry filter paper in a drying oven.

About 5 g. of the acetyl derivative are then saponified by boiling with an accurately measured quantity of alcoholic potassium hydroxide, as described under the determination of the saponification value (p. 114). The alcohol is evaporated off, the soap dissolved in water and a quantity of $N/1$ sulphuric acid added, equivalent to the alcoholic potash used. On careful warming, the fatty acids separate as an oily layer, which is then filtered off and washed with boiling water until the washings are no longer acid. The filtrate is then titrated with $N/10$ alkali. The number of cubic centimetres required is multiplied by 56·1 and divided by the weight of substance. Triglycerides which contain no hydroxy-acids and no soluble fatty acids give no acetyl value. Triglycerides of hydroxylated fatty acids give the values required by theory, hence the acetyl value is in this case a *characteristic* of the fat.

Triglycerides which contain hydroxy-acids, and at the same time also soluble fatty acids, give acetyl values which include also the soluble acids. In order to obtain the *true* acetyl value, the quantity of alkali required to neutralise the soluble acids (which must be determined by a blank experiment) must be subtracted from the *apparent* acetyl value, as determined above. In this case also the acetyl value is a *characteristic*.

In the natural oils and fats, however, which contain varying quantities of free fatty acids, and hence also varying quantities of monoglycerides and diglycerides, the acetyl value is a *variable*, as its value depends not only on the presence of hydroxy-acids, but also on

[1] *J. Soc. Chem. Ind.*, 1897, **16**, 503.

the amount of monoglycerides and diglycerides present. The natural oils and fats contain also small quantities of free alcohols, which also contribute in some degree to the acetyl value. As oxidised acids (see p. 139) also give acetyl values, the acetyl value is very probably a measure of the rancidity of an oil or fat.[1]

(b) Variables.

The following variables are considered here :—
1. The Acid Value.
2. The content of Glycerol.
3. The Unsaponifiable Matter.

1. Determination of the Acid Value.

The acid value indicates the number of milligrams of potassium hydroxide required to neutralise the free fatty acids in 1 g. of fat or wax.

The acid value is thus a measure of the free fatty acids in a fat or wax. For the determination an accurately weighed quantity—as a rule not less than 5 g.—is mixed with neutral (or neutralised) alcohol, or dissolved in a mixture of alcohol and ether, and titrated with aqueous or alcoholic potassium hydroxide, with phenolphthalein as indicator.

The acid value is calculated as shown in the following example :—

Example.—For the neutralisation of the free fatty acids in 6.508 g. of tallow, 3.5 c.c. of $N/10$ potassium hydroxide were required, corresponding to 3.5×5.61 mg. KOH. The quantity required for 1 g. is therefore $\dfrac{3.5 \times 5.61}{6.508} = 3.01$.

The acid value is frequently expressed in per cent. of oleic acid; it is then sufficiently accurate to give half the acid value as the percentage of free fatty acid.

Older methods of calculating take as units, in some cases, the quantity of acid calculated as sulphuric acid; in others, the "degrees of acidity," that is, the number of cubic centimetres of normal alkali required to neutralise 100 g. of fat. The following Table facilitates the conversion of one term into any other :—

Acid value.	Oleic acid.	SO$_3$.	Degrees of acidity.
	Per cent.	Per cent.	
1·0	0·5036	0·0714	1·7857
1·9857	1·0	0·142	3·5458
14·0	7·042	1·0	25·0
0·56	0·2817	0·04	1·0

[1] *Cf.* Lewkowitsch, *Chemical Technology and Analysis of Oils, Fats, and Waxes*, vol. i., p. 435.

In the literature on fats the acid value is much too frequently considered as a "characteristic" (constant). This is entirely misleading, as the acid values of the natural oils and fats, and perhaps also of the waxes, are dependent upon the purity of the sample, the age, the degree to which hydrolysis has occurred, and any oxidation which has taken place. The acid value may therefore vary from 0 to the maximum of about 195 for any fat; the latter value would correspond to 100 per cent. of free fatty acids, which number the author has, in fact, found in the case of a very old palm oil.

The designation of the "ether value" or "ester value" (that is, the difference between the saponification value and the acid value) as a "characteristic" (constant) is equally misleading.

2. Determination of the content of Glycerol.

If the natural oils and fats were neutral triglycerides, the quantity of glycerol could be calculated from the saponification value according to the following equation :—

$$C_3H_5(OR)_3 + 3KOH = C_3H_8O_3 + 3KOR.$$
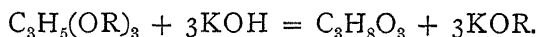
In this case the glycerol content would form a "characteristic." As, however, the majority of the natural oils and fats contain free fatty acids, and hence in all probability mono- and diglycerides, the glycerol content varies, and must therefore be considered as a "variable."

The determination of glycerol in oils and fats is best effected indirectly by the acetin method, as the glycerol obtained by the saponification of a fat invariably contains organic impurities, which give abnormally high values when the glycerol is determined by oxidation (by permanganate or bichromate).

For the acetin method, a crude glycerin must first be prepared. For this purpose, 20 g. of the sample are saponified with alcoholic potash as described under the determination of the saponification value (p. 114), and the alcohol evaporated off on the water-bath. The resulting soap is dissolved in water, and decomposed by sulphuric acid, so that the precipitated fatty acids may be filtered off. The filtrate is treated with excess of barium carbonate, and evaporated on the water-bath until the bulk of the water is driven off. The residue is then extracted with a mixture of ether and alcohol (1 : 3), the bulk of the ether-alcohol evaporated off by careful heating on the water-bath, and the residue dried in a desiccator and weighed. It is not necessary to dry to constant weight, as the glycerol in the crude product is accurately determined by the acetin method.

This method depends upon the complete conversion of glycerol to triacetin on boiling with acetic anhydride, and the subsequent hydrolysis of the product with sodium hydroxide. The acetic acid thus formed is

a measure of the amount of glycerol. The crude glycerol obtained as above is heated to boiling with 8-10 c.c. of acetic anhydride and 4 g. of sodium acetate, in a round-bottomed flask of about 100 c.c. capacity, under a reflux condenser, for one and a half hours. It is then allowed to cool a little, the condenser rinsed out with hot water, and the acetin brought into solution by gentle agitation. If necessary, the contents of the flask may be gently heated, but must not be boiled, as triacetin is volatile with steam. The liquid is filtered from a flocculent precipitate which separates into a wide-necked flask of about 500-600 c.c. capacity, and allowed to cool to the ordinary temperature. Phenolphthalein is added, and the acetic acid neutralised with sodium hydroxide of about 5 per cent. strength. During the addition of the alkali the flask must be continually shaken round so that there is never any local excess of alkali. The neutral point is reached when the pale yellow colour just becomes reddish-yellow. The addition of so much alkali that a red colour is formed must be avoided. If an excess has been accidentally added, so that the neutral point has been overstepped, the experiment must be rejected. With practice the colour change can be easily observed. Exactly 25 c.c. of sodium hydroxide solution of about 10 per cent. strength are then added, the strength of this solution being determined by a blank experiment, and the solution is boiled for a quarter of an hour. The free alkali in both experiments is then titrated back with $N/1$ hydrochloric acid; that is, the total alkali in the blank experiment, and the excess of alkali in the experiment proper. The difference gives the amount of alkali required for the saponification of the triacetin.

Example.—1·5064 g. crude glycerin weighed out. 25 c.c. sodium hydroxide solution required in the blank experiment, 53·0 c.c. $N/1$ hydrochloric acid, and in the actual experiment, 14·7 c.c. $N/1$ hydrochloric acid for the back-titration. Hence, $53·0 - 14·7 = 38·3$ c.c. were required for the saponification of the triacetin. Since 1 c.c. $N/1$ hydrochloric acid corresponds to $\frac{0·092}{3} = 0·03067$ g. glycerol, the crude glycerin contained $0·03067 \times 38·3 = 1·1746$ g. glycerol ($= 77·97$ per cent. glycerol). The 20 g. fat originally taken for the test contained, therefore, 1·1746 g. glycerol, or 5·87 per cent.

A direct method for the determination of glycerol, proposed by A. Shukoff and P. Schestakoff,[1] by extraction of a solution containing at least 40 per cent., has not yet met with general acceptance on account of its tediousness.

3. Determination of the Unsaponifiable Matter.

The term "unsaponifiable matter" comprises all those substances

[1] *Z. angew. Chem.,* 1905, **18**, 294; *J. Soc. Chem. Ind.,* 1905, **24**, 294.

which are insoluble in water, or which do not form soluble soaps with caustic alkalis. The natural oils and fats always contain small quantities of unsaponifiable matter.

The unsaponifiable matter is separated as such, and to this end the fat must first be saponified. It is convenient to combine the determination of the unsaponifiable matter with that of the saponification value; it must, however, be borne in mind, that in view of the very small quantity of unsaponifiable matter, it is necessary to take at least 5 g. for the test. The procedure is as follows :—5 g. of the sample are saponified with 25 c.c. of alcoholic sodium hydroxide, containing 80 g. of sodium hydroxide per litre, by heating on a water-bath in a porcelain dish, and evaporated to dryness. The soap is dissolved in 50 c.c. of hot water, transferred to a separating funnel of about 200 c.c. capacity, and the residual contents of the dish rinsed into the separator with 20-30 c.c. of water. After cooling, about 50 c.c. of ether are added, and the whole is well shaken. If the layers do not separate readily, a little alcohol or concentrated sodium hydroxide is added. The clear soap solution is run off into a second separating funnel and shaken out again with ether. The ethereal extracts are combined, washed with a little water, and transferred to a weighed flask. The ether is evaporated off on the water-bath, the residue dried at 100°, and weighed. In the case of most oils and fats, ether is preferable to petroleum spirit for the extraction.

This method is not suitable for determining the unsaponifiable matter in beeswax, carnaüba wax, and other solid waxes, as not only are the alcohols derived from these esters sparingly soluble in cold ether, but also the alkali salts of the fatty acids do not dissolve easily in water, nor even in dilute alcohol. In such cases it is advisable to neutralise the soap solutions, after adding phenolphthalein, with acetic acid, and to precipitate with either barium chloride or lead acetate. The precipitate is then washed, dried, mixed with sand in a mortar, and extracted in a Soxhlet apparatus with petroleum spirit boiling below 80°.

A characteristic component of the unsaponifiable matter of vegetable oils and fats is sitosterol or other closely allied phytosterols; the unsaponifiable residue of animal oils and fats, on the other hand, contains cholesterol. A further examination of the unsaponifiable matter is imperative when it is necessary to distinguish between vegetable and animal fats (see p. 139).

II. QUALITATIVE METHODS.

The following qualitative methods of examination frequently yield important clues for the detection and valuation of individual oils and fats, and must be used to supplement the quantitative reactions, when

the latter fail to give definite indications. A number of qualitative reactions have become superfluous since the method of determining the iodine value has come into use, *e.g.*, the elaidine test, the sulphur chloride test, and also the thermal reactions with sulphuric acid, bromine, and sulphur chloride. Only the following methods need therefore be described :—

> 1. Oxygen absorption.
> 2. Bromide test.
> 3. Colour reactions.

1. Oxygen Absorption.

The absorption of atmospheric oxygen is of great importance in judging the danger of spontaneous combustion when oils are distributed in a finely divided condition on organic fibres (*cf.* "Wool oils," p. 160) ; it is generally determined in the case of drying oils. The methods used for this purpose are mostly "practical" tests ; these are described in the following Section (p. 165).

If a convenient method for the determination of the total oxygen absorbed during drying were available, it would be possible to obtain a quantitative expression of the drying properties, or as it might be termed, of the "oxygen value." Quantitative determinations have in the past been made, but in a very unsystematic fashion, such important factors as the temperature, the influence of light, the moisture of the air, the thickness of the layer, and the age of the oil having been more or less ignored.

As the drying of an oil requires a somewhat lengthy period of time, attempts have been made to accelerate the absorption of oxygen, by adding finely divided lead ("molecular" lead) (A. Livache[1]), or finely divided copper (Hübl, Lippert[2]). The lead powder is obtained by precipitating a lead salt by means of zinc. The precipitate is washed with water, alcohol, and ether in rapid succession, and finally dried in a vacuum. Livache's test is carried out as follows :—1 g. of the lead powder is spread out in a thin layer on a fairly large watch-glass, and 0·6-0·7 g. (not more) of the oil allowed to drop on to the powder, care being taken to let each drop fall on to a separate place on the lead (or copper) powder, and not to allow the drops to run together. The watch-glass is then allowed to stand at the ordinary temperature in the light. Linseed oil attains its maximum absorption in a few days, whereas under other conditions the same result is obtained only after a prolonged time. Livache states that drying oils attain their maximum absorption in eighteen hours, or in some cases after three days, whereas non-drying oils show an increase of weight only after four to five days.

[1] *Comptes rend.*, 1886, **102**, 1167 ; *J. Soc. Chem. Ind.*, 1886, **4**, 494.
[2] *Chem. Revue*, 1899, p. 67.

Weger[1] rejects Livache's method and suggests the use of larger quantities of lead, 2 g. of lead being used for each 0·2 g. of oil. But even under these conditions the results are unsatisfactory.

M. Weger[2] and also W. Lippert[3] have undertaken a systematic study of the drying properties of oils, the oils being exposed to the air in extremely thin layers on glass plates. It was shown that the glass plates could not be replaced by any other lighter material; plates of celluloid, gelatin, and even ebonite were found altogether unsuitable; mica plates were satisfactory but are too easily broken, whilst thin metal plates are too easily deformed. The following precautions are necessary in the experiments:—The glass plate must be quite clean (free from dust), and the oil must be very carefully spread out in a uniform thin layer. If the layer is uneven in thickness, it is possible for an increase of weight to be taking place in one place, whilst a decrease is occurring at another. A series of tests showed that, the thinner the layer of oil, the more rapidly the oxygen is absorbed at the commencement of the experiment, whilst an equilibrium sets in after about twenty-four hours. The thicker the layer, the more slowly the weight increases; but if the layer is altogether too thin, unreliable results are obtained. The best conditions for the absorption of oxygen seem to be reached when the layer of oil is so thin that 0·0005 g. cover 1 sq. cm. of the glass plate.

This method is obviously very tedious, and depends upon the accuracy with which decimilligrams can be weighed; moreover, it does not yield absolute data, and can only be used as a guide in comparative experiments. If it is only a question of distinguishing between drying, semi-drying, and non-drying oils, the determination of the iodine value (p. 116) is not only more easily carried out, but has also the advantage of giving quantitative results. At the same time, it must be emphasised that the iodine value is not an absolute measure of the drying properties; for fish oils and liver oils add just as much iodine as the best drying oils, and yet absorb much less oxygen. Furthermore, the former are distinguished essentially from the latter in that they do not form a skin as linseed oil does. Fish oils and liver oils are, however, best distinguished from the drying oils by the bromide test (cf. p. 137).

2. The Bromide Test.

On the basis of Hazura's work on the action of bromine on unsaturated acids, O. Hehner and C. Mitchell[1] proposed the following

[1] *Chem. Revue*, 1898, p. 246.

[2] *Chem. Rev. Fett-Ind.*, 1897, 4, 313, 327; *J. Soc. Chem. Ind.*, 1898, 17, 257, 360.

[3] *Chem. Rev. Fett-Ind.*, 1899, 6, 65; *J. Soc. Chem. Ind.*, 1899, 18, 693.

[4] *Analyst*, 1898, 23, 313.

test, which is described with certain modifications which have been worked out in the author's laboratory :—1-2 g. of the oil are dissolved in 40 c.c. of ether with the addition of a few cubic centimetres of glacial acetic acid. The solution is cooled in a corked flask to 5°, and bromine then added, drop by drop, from a drawn-out tube, until the brown colour no longer disappears. After standing for three hours at 5°, the liquid is filtered through a pleated filter and washed four times successively with 10 c.c. of ether cooled to 0°. The residue is finally dried in a water-oven to constant weight. In the following Table a number of results obtained by this test are collated, of which some are given by Hehner and Mitchell, and the remainder obtained by the author and his assistants, Walker and Warburton.

The bromide test is especially adapted to the testing of drying oils and fish oils. It is still better to apply it to the fatty acids, as it is possible in this way to distinguish between vegetable drying oils and fish oils (cf. p. 137).

Table 21.
Yield of Hexabromides from Glycerides.

Oil.	Yield of bromides insoluble in ether.	Observer.
	Per cent.	
Linseed oil (iodine value 181) . .	23·14 ; 23·52	Walker and Warburton
,, (,, 186·4) .	24·17	Lewkowitsch
,, (,, 190·4) .	37·72	,,
,, ...	23·86 to 25·8	Hehner and Mitchell
Tung oil	0	,,
,, (sample 1) . . .	0	Walker and Warburton
,, (,, 2) . . .	0·38 ; 0·39	,,
Candle nut oil	8·21 ; 7·28	,,
Walnut oil	1·42 ; 1·9	Hehner and Mitchell
Poppy seed oil	0	,,
Soya bean oil	3·73	Lewkowitsch
Maize oil	0	Hehner and Mitchell
Cotton seed oil	0	,,
,, ...	0	Lewkowitsch
Brazil nut oil	0	Hehner and Mitchell
Almond oil	0	,,
Olive oil	0	,,
Japan fish oil	21·14 ; 22·07	Walker and Warburton
Fish oil deodorised . . .	49·01 ; 52·28	,,
Cod liver oil	42·9	Hehner and Mitchell
,, ...	35·33 ; 33·76	Walker and Warburton
,, (Newfoundland) .	32·68 ; 30·62	,,
Shark liver oil	22	Hehner and Mitchell
,, ...	21·22 ; 19·08	Walker and Warburton
Seal oil	27·54 ; 27·92	,,
Whale oil	25	Hehner and Mitchell
,, (old) . .	15·54 ; 16·14	Walker and Warburton
,, (fresh) . .	20·1 ; 22·6	Lewkowitsch
Sperm oil	2·61 ; 2·42	Walker and Warburton
,, ...	3·72 ; 3·69 after standing for 48 hours	,,

3. Colour Reactions.

Of the almost innumerable colour reactions which have been proposed, and are still being proposed, only the following, as the author has shown by extensive tests, can be recommended as trustworthy and of practical value.[1]

(a) *H. Baudouin's Test.*—This reaction, originally introduced by Camoin, is used for the detection of sesamé oil, certain components of which give a characteristic red colour with hydrochloric acid and cane sugar. As cane sugar is converted by hydrochloric acid into levulose and furfural, Villavecchia and Fabris have suggested the following method of carrying out the test:—A solution of 1 vol. of colourless furfural in 100 vols. of absolute alcohol is made up, and to 0·1 c.c. of this solution, 10 c.c. of the sample, and 10 c.c. of hydrochloric acid of sp. gr. 1·19 are added, the whole well shaken and allowed to settle. If the sample contains even less than 1 per cent. of sesamé oil, the lower aqueous layer shows a distinct crimson-red colour. In case colouring matters are present in the fat, which give a coloration with hydrochloric acid alone, these should be removed first by shaking the sample with concentrated hydrochloric acid. The only objection to this treatment is that it is sometimes necessary to repeat the shaking so many times that the chromogenetic substance in sesamé oil is also destroyed.

(b) *Halphen's Test.*—This indicates cotton seed oil. Equal volumes of the sample, amyl alcohol, and carbon bisulphide containing 1 per cent. of flowers of sulphur in solution, are heated for fifteen to thirty minutes in a test tube in a water-bath or salt water-bath for fifteen to thirty minutes. In presence of cotton seed oil a characteristic red colour is obtained. The value of this test must not be overestimated since on the one hand cotton seed oil, which has been previously heated to 180°-250°, fails to give the reaction, and on the other hand when cattle are fed with cotton seed oil cakes or cotton seeds, the chromogenetic substance passes into the milk fat; it also passes into lard, when hogs have been fed with cotton seed or cotton seed oil cakes. It must also be noted that kapok oil and baobab oil also give this reaction. Recently E. Gastaldi[2] has shown that only commercial amyl alcohol produces the colour, which is therefore produced by impurities in the amyl alcohol. Pyridine and allied bases give the colour reaction very distinctly.

(c) *Becchi's Test* (Silver nitrate test).—This test for cotton seed oil is less reliable than Halphen's. It is most trustworthy when carried out as proposed by Tortelli and Ruggeri: 5 g. of the sample are

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[1] *J. Soc. Chem. Ind.*, 1894, **13**, 617 ; also Lewkowitsch, *Chemical Technology and Analysis of Oils, Fats, and Waxes*, vol. i., pp. 398 *et seq.*

[2] *Ann. Lab. Gabelle*, 1912, **6**, 601 ; *J. Soc. Chem. Ind.*, 1912, **31**, 934.

saponified and the liquid fatty acids are isolated (*cf.* p. 134); these are dissolved in 10 c.c. of 95 per cent. alcohol, 1 c.c. of a 5 per cent. solution of silver nitrate added, and the solution warmed to 70°-80°. In presence of cotton seed oil, the silver nitrate is at once reduced, whereas other oils reduce it only after a considerable time.

(d) *The Nitric Acid Test* is frequently useful as a preliminary indication of cotton seed oil. A few cubic centimetres of the sample are shaken with an equal volume of nitric acid of sp. gr. 1·375 and allowed to stand for some time (up to twenty-four hours). In presence of cotton seed oil a coffee-brown colour is observed, which is still produced by heated cotton seed oil and its fatty acids (which, as stated above, fail to give the Halphen reaction).

The three last-mentioned colour reactions for the detection of cotton seed oil must be used with the greatest circumspection, and must be considered at the best only as confirmatory tests.

(e) *Liebermann-Storch Test.*—This colour reaction is extremely trustworthy for the detection of rosin oils. A quantity of 1-2 c.c. of the sample is dissolved in acetic anhydride with moderate warming; after cooling a drop of sulphuric acid of sp. gr. 1·53 (prepared by mixing 34·7 c.c. of concentrated sulphuric acid with 35·7 c.c. of water) is added. In presence of rosin acids a beautiful violet-red fugitive colour is obtained. Cholesterol also gives a similar colour. If the latter is suspected the rosin acids must be separated from the unsaponifiable cholesterol. The best method for the detection of cholesterol is described below (p. 139).

(f) *The Sulphuric Acid Test.*—All the colour reactions with sulphuric acid given in the older literature are unreliable, with the exception of the reaction for the detection of liver oils.

To carry out the test 1 drop of the oil is dissolved in 20 drops of carbon bisulphide, and a drop of concentrated sulphuric acid is added. If liver oils are present a violet-blue colour is produced, which quickly changes to red and brown. The colour seems to be produced not only by cholesterol but also by "lipochromes."

C.—EXAMINATION OF THE FATTY ACIDS.

In case the methods described above have not given sufficient information for the identification of a sample, the free fatty acids must be examined. For this purpose physical methods such as the determination of the solidifying point (titre) (*cf.* the following Section, p. 174, and Tables, p. 146) are used, but more especially the following chemical methods, which are to some extent based upon the above quantitative reactions.[1]

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[1] For further methods, *cf.* Lewkowitsch, *Chemical Technology and Analysis of Oils, Fats, and Waxes*, vol. i., chap. viii.

1. Determination of the Neutralisation Value, from which the mean molecular weight can be derived.

2. Determination of Lactones (Anhydrides).

3. Determination of Insoluble Fatty Acids.

4. Determination of Soluble Fatty Acids.

5. Separation of Saturated Fatty Acids from Unsaturated.

6. Examination of the Saturated Fatty Acids.

7. Determination of Oleic, Linolic, Linolenic, and Clupanodonic Acids.

8. Determination of the "Oxidised" Fatty Acids.

The free fatty acids are prepared as described in the following Section under the "determination of the titre of tallow," p. 174). The soluble volatile fatty acids need only be taken into consideration in the case of oils and fats whose saponification value exceeds 200.

If great accuracy is desired, the unsaponifiable matter should be removed with ether, before decomposing the soap solution with mineral acid (see p. 124).

1. Determination of the Neutralisation Value and the Mean Molecular Weight.

The neutralisation value indicates the number of milligrams of potassium hydroxide required to saturate 1 g. of the mixed fatty acids.

The determination of the neutralisation value is carried out in exactly the same manner as described under "acid value" (p. 122), but using aqueous normal alkali. It is advisable to take at least 5 g. of the sample for the determination. Deductions as to the approximate composition of a mixture of fatty acids may be obtained from the following Table (cf. also the Tables given on pp. 146 et seq.).

From the neutralisation value thus found, the mean molecular weight is calculated as follows :—Let M be the mean molecular weight of the fatty acid; then M grams must, according to theory, be neutralised by 56·1 g. potassium hydroxide. If n be the number of grams of potassium hydroxide which have been shown by experiment to neutralise 1 g. of fatty acid, then the proportion M : 56·1 = 1 : n, and hence M = $\frac{56·1}{n}$. The value of n is found by multiplying the number of cubic centimetres of normal alkali required for 1 g. fatty acid by 0·0561. If this number of cubic centimetres be a then $n = a \times 0·0561$. Introducing this into the above equation :—

$$M = \frac{56·1}{a \times 0·0561} = \frac{1000}{a}.$$

Table 22.

Neutralisation Values of Fatty Acids.

Acid	Formula.	Molecular weight.	Neutralisation value.
Acetic	$C_2H_4O_2$	60·03	934·5
Butyric . . .	$C_4H_8O_2$	88·06	637·07
Caproic . . .	$C_6H_{12}O_2$	116·10	483·22
Caprylic . . .	$C_8H_{16}O_2$	144·13	389·23
Capric	$C_{10}H_{20}O_2$	172·16	325·85
Lauric	$C_{12}H_{24}O_2$	200·19	280·30
Myristic . . .	$C_{14}H_{28}O_2$	228·22	245·81
Palmitic . . .	$C_{16}H_{32}O_2$	256·26	218·90
Stearic	$C_{18}H_{36}O_2$	284·29	197·33
Oleic	$C_{18}H_{34}O_2$	282·27	198·74
Linolic . . .	$C_{18}H_{32}O_2$	278·24	200·17
Linolenic . . .	$C_{18}H_{30}O_2$	280·26	201·62
Clupanodonic . .	$C_{18}H_{28}O_2$	276·22	203·09
Ricinoleic . .	$C_{18}H_{34}O_3$	298·29	188·08
Arachidic . . .	$C_{20}H_{40}O_2$	312·32	179·62
Erucic	$C_{22}H_{42}O_2$	338·34	165·81
Cerotic . . .	$C_{26}H_{52}O_2$	396·42	141·52
Melissic . . .	$C_{30}H_{60}O_2$	452·48	123·98
Hydroxystearic . .	$C_{18}H_{36}O_3$	300·29	186·81
Dihydroxystearic . .	$C_{18}H_{36}O_4$	316·29	177·33
Trihydroxystearic .	$C_{18}H_{36}O_5$	332·29	168·82
Sativic	$C_{18}H_{36}O_6$	348·29	161·07
Linusic . . .	$C_{18}H_{36}O_8$	380·29	147·51

2. Determination of Lactones (Anhydrides.)

If the free fatty acids, instead of being examined for their neutralisation values as described above, are boiled with excess of alcoholic potash as in the determination of the saponification value (p. 114), the same value should be obtained, or in other words, the saponification number of a fatty acid should be identical with its neutralisation value on the assumption that the amount of unsaponifiable matter is negligible. If, however, the fatty acids contain lactones or anhydrides, the saponification value will be greater than the neutralisation value. The difference forms a measure of the lactones or anhydrides present. Its determination is of importance in the examination of candle materials (see next Section, p. 173).

3. Determination of Insoluble Fatty Acids.

For this determination the fat is filtered, and 3-5 g. are saponified as described under "saponification value" (p. 114), using, of course, a flask of double the capacity given above. The alcohol is then completely evaporated off, until the soap solution becomes thick. Then 100-150 c.c. of hot water are added, the solution acidified with dilute sulphuric acid, and heated until the liberated fatty acids float on the surface as a clear

oily layer.   The solution is next filtered through a filter paper of about
10 cm. diameter, previously dried at 100° and weighed, taking care first to
fill the filter paper half full of hot water.   The liquid is then brought on to
the filter, keeping it half full throughout the operation.   The fatty acids
are washed with hot water on the filter, until a few cubic centimetres of
the filtrate no longer redden sensitive litmus paper.   In the case of
fats of the cocoa nut oil and dika fat groups, 2 or 3 l. of water are
sometimes necessary.   On the completion of the washing the funnel and
filter are immersed in cold water, so that the liquid in the filter and the
water outside are at the same level.   This causes most fatty acids
to solidify.   The water is allowed to drain off, the filter brought into a
small weighed beaker and dried for two hours at 100°.   After weighing,
the drying is continued for an hour, and the weighing repeated.   The
difference between the two weights does not usually exceed 1 mg.;
absolute constancy cannot be expected, as there are two sources of
error, which, however, usually compensate one another.   On the one hand
unsaturated fatty acids become slightly oxidised, and on the other hand
they volatilise to some extent.   The fatty acids of highly unsaturated
oils are best washed with ether into a tared flask, and dried in a current
of carbon dioxide or hydrogen.

Most fats give a yield of 95 per cent.; only those fats which have
high Reichert values yield less than 95 per cent.   It must be borne in
mind that any unsaponifiable matter is weighed with the acids, and that
the yield cannot therefore be identified with the percentage of fatty
acids.   In most oils and fats the proportion of unsaponifiable matter
may, as a rule, be neglected, but in accurate analyses this must
be determined as described on p. 124, and deducted.   In the case
of waxes, the alcohols separate out together with the fatty acids, and
thus results exceeding 100 per cent. are obtained.

4. Determination of Soluble Fatty Acids.

A high Reichert-Meissl value points to the presence of considerable
quantities of volatile fatty acids.   The volatile fatty acids—comprising
butyric, caproic, caprylic, capric, and lauric acids—are conveniently
subdivided into soluble volatile acids and insoluble volatile acids,
although a sharp analytical distinction between these two classes cannot
be drawn.   The Reichert-Meissl method estimates a *part* of the soluble
volatile fatty acids (almost all the butyric acid, part of the caproic, and
a little caprylic acid).   Similarly Polenske's method which is carried out
in conjunction with the Reichert-Meissl method (see p. 156) gives
approximately the insoluble volatile acids (comprising very little butyric
acid, a little caproic, more caprylic, almost all the capric and all the
lauric acid which has passed over, together with traces of myristic acid).
In the analysis of butter fat for the detection of fats of the cocoa nut oil

group, the determination of both groups of acids and of their mean molecular weight leads to important results.[1]

5. Separation of Saturated from Unsaturated Fatty Acids.

The best method (though still an incomplete one) for this separation is based upon the solubility of the lead salts of unsaturated fatty-acids in ether, in which the lead salts of the solid fatty acids are almost insoluble. This method is most trustworthy when carried out in the following manner worked out in the author's laboratory. The method depends upon a combination of the modifications proposed by Muter and de Koningh, and by Lane, to a method originally devised by Gusserow and Varrentrapp.

From 3-4 g. of the fatty acids are neutralised in the usual manner in a 300 c.c. flask, with 50 c.c. of about $N/2$ aqueous potassium hydroxide. (If the determination is started with the original fat this must be boiled with alcoholic potash to saponify it. After adding phenolphthalein the solution is rendered faintly acid with acetic acid, and finally exactly neutralised with alcoholic potash). The solution is made up to about 100 c.c. with water. A solution prepared from 30 c.c. of a 10 per cent. solution of lead acetate and 150 c.c. of water, is then heated to boiling in a beaker, and poured, whilst boiling hot, into the soap solution, shaking continuously, so that the precipitated lead soaps may deposit themselves on the walls of the flask. The flask is filled to the neck with hot water and allowed to cool. After the liquid has become clear it is poured off or filtered if necessary. The lead soaps are carefully washed with hot water. It is advisable to cool the hot solutions before filtering, thus causing the cooled lead soaps to adhere to the sides of the flask. The last traces of water are removed by means of a small roll of filter paper. It is not advisable to dry the lead salts, as in the case of drying oils they absorb oxygen somewhat rapidly from the air. Next 150 c.c. of ether are added to the lead salts, the flask corked and shaken repeatedly, so as to disintegrate the lead salts. The flask is then attached to a reflux condenser, and heated on a water-bath for some little time with frequent shaking. The lead salts of the liquid fatty acids dissolve readily in the hot ether; at the same time a certain quantity of the saturated acids pass into solution. When the undissolved salts settle out at the bottom of the flask as a fine powder, the heating is discontinued. If all operations are conducted somewhat rapidly, and unnecessary exposure to the air is avoided, it is not essential to work in an atmosphere of hydrogen or carbon dioxide. The ethereal solution is allowed to cool, and filtered through a pleated filter covered with a watch glass, into a separating funnel. The undissolved salts are brought

[1] Cf. Lewkowitsch, *Chemical Technology and Analysis of Oils, Fats, and Waxes*, vol. i., p. 538.

on to the filter by rinsing out the flask three or four times with ether, using 30-40 c.c. each time. The ethereal filtrate is then shaken with dilute hydrochloric acid to decompose the lead soaps. The ether dissolves the free fatty acids as they form, and the undissolved lead chloride and aqueous solution are drawn off. The ethereal solution is washed with water until the wash water ·is free from acid. Finally the

Table 23.

The Iodine Value of Unsaturated Fatty Acids and their Glycerides.

Acid.	Formula.	Iodine value of fatty acid.	Iodine value of		
			Mono-glyceride.	Di-glyceride.	Tri-glyceride.
Tiglic	$C_5H_8O_2$	253·68	145·79	198·18	225·10
,, ...	$C_{12}H_{22}O_2$	128·88	93·26	112·22	120·39
,, ...	$C_{14}H_{26}O_2$	112·21	85·54	99·84	106·26
Hypogæic . . .					
Physetoleic . .	$C_{16}H_{30}O_2$	99·84	77·32	89·93	95·10
Lycopodic . . .					
Oleic					
Elaidic . . .	$C_{18}H_{34}O_2$	89·92	71·24	81·80	86·06
Rapic. . . .					
Doeglic . . .					
Jecoleic . . .	$C_{19}H_{36}O_2$	85·67	68·54	78·28	82·15
Erucic . . .					
Brassidic . . .	$C_{22}H_{42}O_2$	75·02	61·55	69·23	72·31
Linolic . . .					
Tariric . . .					
Telfairic . . .	$C_{18}H_{32}O_2$	181·14	143·28	164·68	173·31
Elæomargaric . .					
Linolenic . . .					
Isolinolenic . .	$C_{18}H_{30}O_2$	273·69	216·16	248·65	261·76
Jecoric . . .					
Clupanodonic . .	$C_{18}H_{28}O_2$	366·24	289·04	332·63	350·23
Isanic . . .	$C_{14}H_{20}O_2$	461·19	345·11	409·12	436·08
Ricinoleic . .					
Isoricinoleic . .	$C_{18}H_{34}O_3$	85·13	68·17	77·79	81·37
Ricinelaidic . .					
Ricinic . . .					
Mixed Triglycerides :—					
Myristopalmito-olein . .	...	...	...	...	31·54
Oleodipalmitin . . .	...	...	...	...	30·43
Oleodimargarin . .	...	...	...	...	29·48
Oleopalmitostearin . .	...	...	...	...	29·48
Oleodistearin . . .	...	...	...	..	28·55
Elaidodistearin . . .	...	. .	...	...	28·55
Dioleostearin . . .	...	...	...	...	57·24

ether solution is filtered through a small pleated filter into an ordinary flask. In case the liquid fatty acids consist chiefly of oleic acid, the results will be accurate enough if the ether be evaporated off on the water-bath, and the residue dried in a water-oven. If, however, more highly unsaturated acids than oleic are suspected (from linseed oil, soya-bean oil, maize oil, marine animal oils), the ethereal solution must be

evaporated down in a current of dry hydrogen or dry carbon dioxide. The precipitate collected on the filter consists of the soaps of the saturated fatty acids; the free acids are obtained by decomposing these soaps with hydrochloric acid in the manner described above.

It must be especially emphasised that this method of separation is not absolutely accurate; thus the solid fatty acids always retain unsaturated acids (the quantity of which can be estimated approximately by the iodine value). Moreover, the ethereal solution of the lead salts retains a certain quantity of saturated fatty acids, especially the volatile fatty acids. Nevertheless the method gives results which are sufficiently accurate for the ordinary purposes of technical analysis. It is advisable to estimate the iodine value of the liquid fatty acids, as this supplies valuable information as to the composition of the fats when the Table on p. 135 is taken as a guide (cf. also under No. 7, p. 137).

6. Examination of the Saturated Fatty Acids.

The only solid fatty acids which can at present be determined with sufficient accuracy are arachidic and stearic acids.

Arachidic Acid.—The determination of this acid is necessary for the recognition of arachis oil in mixtures of oils containing arachis oil (adulterated olive oil). For the estimation, the solid fatty acids obtained from 10 g. of oil are dissolved in 50 c.c. of hot 90 per cent. alcohol. In presence of arachidic acid a crystalline mass is obtained on cooling the alcoholic solution. This consists of "crude arachidic acid," that is a mixture of arachidic and lignoceric acids. The crystals are filtered off and washed, first with a measured quantity of 90 per cent. alcohol, then with 70 per cent. alcohol; the latter dissolves only traces of the acid. The crystals on the filter are finally washed with boiling absolute alcohol, and the filtrate collected in a porcelain dish or a flask. The alcohol is evaporated off and the dried crystals weighed. A correction must be made for the arachidic acid dissolved by the 90 per cent. alcohol, taking as a basis that 100 c.c. dissolve at 15°, 0·022, or at 20°, 0·045 g. crude arachidic acid. Finally, the melting point of the crude arachidic acid is determined; this should be 71°-72°.[1]

Stearic Acid.—The determination of stearic acid depends upon the observation due to David, that alcohol saturated at 0° with pure stearic acid, dissolves all the lower solid fatty acids as also all the unsaturated acids, whereas stearic acid remains undissolved. The method may be applied either to the total fatty acids, or to the saturated fatty acids isolated as described on p. 134. It should, however, be observed that any arachidic acid present must be removed beforehand, as it would

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[1] For details and criticism of a modified method of estimation proposed by Tortelli and Ruggeri, cf. Lewkowitsch, *Chemical Technology and Analysis of Oils, Fats, and Waxes*, vol. ii., p. 253.

otherwise be estimated as stearic acid. O. Hehner and C. Mitchell[1] have worked out a method on this basis, which is applicable in most cases, though, it must be pointed out, not in all. The stearic acid solution is prepared by dissolving 3 g. of stearic acid in 1000 c.c. of hot alcohol of sp. gr. 0·8183 in a stoppered flask. The flask is allowed to remain overnight in ice, and the mother-liquor is syphoned off, without taking the flask out of the ice water. This is done with the aid of a tube widened at the end to a small funnel which dips into the alcoholic solution; the small funnel is covered with fine linen to retain the separated crystals of stearic acid. The filter tube is bent twice at right angles, and fitted to a flask so that the clear liquid may be drawn off quickly by means of a filter pump.

If the fatty acids are solid, 0·5-1·0 g. is taken; if liquid, 5 g. This is weighed accurately in a flask, and treated with 100 c.c. of the above described stearic acid solution. The flask is allowed to stand overnight in ice water. On the next day the liquid is shaken, the flask being still in the ice water, to promote the separation of crystals, and then left in the ice water for another half hour. The alcoholic solution is drawn off as described above, and the precipitate remaining in the flask is washed three times successively with quantities of 10 c.c. of the alcoholic solution cooled to 0°. Finally, the crystals of stearic acid adhering to the filter are washed into the flask with hot alcohol. The alcohol is evaporated off, the residue dried at 100° and weighed, and calculated to pure stearic acid. The melting point of the crystals should not be much below 68°·5. A correction of 0·005 g. is applied for the stearic acid introduced by the alcoholic solution of stearic acid. If the melting point of the isolated acid is below 68°, the acid must be again subjected to the same treatment.

7. Determination of Oleic, Linolic, Linolenic, and Clupanodonic Acids.

From the iodine value of the liquid fatty acids, a preliminary indication as to their nature is obtained. In the present state of our knowledge, the acids which come chiefly into consideration are oleic, linolic, linolenic, and clupanodonic acids. If the iodine value is about 90, this indicates, as a rule, practically pure oleic acid; if, however, the iodine value is much higher, then in the case of vegetable oils the presence of linolic and linolenic acids is indicated, and in the case of marine animal oils, the presence of clupanodonic acid is most probable. In the case of mixtures, the presence of all of these acids is possible. Linolenic and clupanodonic acids are detected by the bromide test, and are estimated quantitatively as follows :—

[1] *Analyst*, 1896, **21**, 321.

A solution of 0.3 g. of the fatty acid in glacial acetic acid is cooled in a corked flask to 5°. Bromine is then added, drop by drop, until the brown colour no longer disappears. Any evolution of hydrogen bromide is caused by too high a temperature. After standing for three hours to permit of complete absorption of the bromine, the solution is filtered through a pleated filter, and washed with four successive quantities of 10 c.c. of cold ether. The residue on the filter is dried to constant weight in a water-oven. The melting point of the bromide lies between 175° and 180°, in the case of the hexabromide of linolenic acid (from drying oils). If the bromide has not melted at 180°, but blackens at 200° or above, it consists of octobromides (from marine animal oils). If the residue be suspected to be a mixture of hexa-bromides and octobromides, these are separated by boiling the residue with benzene, in which the octobromides are insoluble; the two are identified by their melting points after the removal of the benzene.

Linolic acid may be approximately estimated in the filtrate as the tetrabromide by the following method given by K. Farnsteiner. The solution is evaporated and the residue, consisting presumably of a mixture of the dibromide of oleic acid and the tetrabromide of linolic acid, is treated with hot petroleum spirit of boiling point 35°-67°·5. On cooling, a crystalline tetrabromide of linolic acid separates out, whilst a liquid tetrabromide and the dibromide of oleic acid remain in solution. The crystals which are filtered off should melt at about 112°.[1]

The following Table contains a number of determinations carried out in the author's laboratory :—

	Fatty acids from oils.	Bromides insoluble in ether.
		Per cent.
Hexabromides.	Linseed (iodine value 181) . . .	29·06 ; 29·34
	,, (,, 184) . . .	31·31 ; 30·44 ; 30·80
	,, (,, 190·4) . . .	38·1 ; 42·0
	,, liquid acids (iodine value 208) .	34·9
	Candle nut	11·53 ; 11·23 ; 12·63
	Stillingia	25·78
	Safflower	1·65 ; 0·65
	Soya bean	3 to 5
	Rape	2·4 ; 3·4
Octobromides.	Japan fish (old samples) . . .	23·04 ; 23·32
	,, (fresh ,,) . . .	44·2 ; 44·7
	Deodorised fish	38·42 ; 39·27
	Cod liver (Norway)	29·86 ; 30·36
	,, (Newfoundland) . . .	39·1 ; 37·76
	Shark liver	12·68 ; 15·08
	Seal	19·83 ; 19·93
	Whale (old samples) . . .	12·38 ; 12·44
	,, (fresh samples) . . .	22·59 ; 27·77
	Sperm	2·05

[1] For further details cf. Lewkowitsch, *Chemical Technology and Analysis of Oils, Fats, and Waxes*, vol. i., pp. 560 *et seq.*

8. Determination of Oxidised Fatty Acids.

The "oxidised" fatty acids comprise those acids which are present in oxidised oils and fats, and which are distinguished from other fatty acids by their insolubility in petroleum spirit. They are estimated as follows by W. Fahrion's method[1]:—4-5 g. of an oxidised fat or oil are saponified in the usual manner with alcoholic potash. The alcohol is evaporated off, the soap dissolved in hot water, introduced into a separating funnel, and decomposed by hydrochloric acid. After cooling, the liquid is shaken with petroleum spirit (boiling below 80°) and then allowed to stand until it has completely separated into two layers. The insoluble oxidised fatty acids adhere to the walls of the funnel or form lumps under the layer of petroleum spirit. The aqueous solution is drawn off, the petroleum spirit layer decanted, and the oxidised fatty acids again well shaken with petroleum spirit to wash out all occluded soluble fatty acids. If the quantity of oxidised acid is large, it is advisable to dissolve it in potassium hydroxide solution, decompose the soap again with hydrochloric acid, and shake out as before with petroleum spirit. The residual oxidised acids are dissolved in warm alcohol, the solution brought into a tared dish, the alcohol evaporated off, and the residue dried to constant weight.[2]

D.—EXAMINATION OF UNSAPONIFIABLE MATTER.

The unsaponifiable matter, which is isolated in substance as described above (p. 124), can be further examined immediately. If the samples have not been adulterated with mineral oils, rosin oil, or tar oil, the quantity of unsaponifiable matter will be very small, as the unsaponifiable substances which occur naturally in oils and fats amount generally to less than 1 per cent. (*cf.* above, p. 124). In waxes, however, the quantity is much greater—up to 50 per cent. The examination of the unsaponifiable matter may be divided into :—

I. The examination of those unsaponifiable substances which are naturally present.

II. The detection and estimation of unsaponifiable substances which have been added purposely.

1. The Examination of Unsaponifiable Substances which are Naturally Present.

(a) In Oils and Fats.

The unsaponifiable matter in natural oils and fats contains chiefly cholesterol or phytosterol, accompanied by small quantities of hydro-

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[1] *Z. angew. Chem.*, 1898, **11**, 781 ; 1903, **16**, 79, 1199 ; *J. Soc. Chem. Ind.*, 1898, **17**, 958 ; 1904, **23**, 26.
[2] For the further examination of these acids, *cf.* Lewkowitsch, *Chemical Technology and Analysis of Oils, Fats, and Waxes*, vol. iii., p. 468.

carbons, higher aliphatic alcohols, colouring matters, resinous substances, and albuminous matter. Since, as shown above, "cholesterol" is characteristic of animal oils and fats, and "phytosterol" (mostly sito-sterol) is characteristic of vegetable oils and fats, the examination of the unsaponifiable matter supplies a means of distinguishing between animal and vegetable products. If the sample consist of a mixture of animal and vegetable fats, both alcohols will be found in the residue.
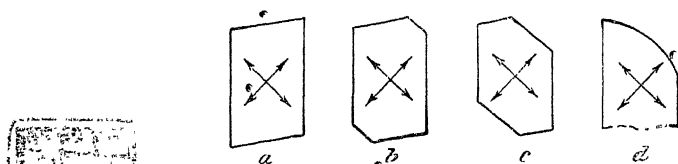
FIG. 37.—Crystals of Cholesterol.
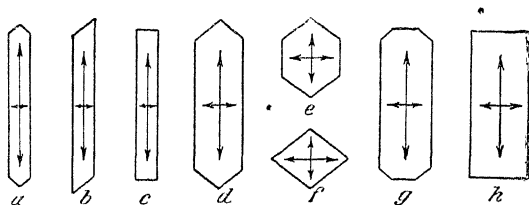
FIG. 38.—Crystals of Phytosterol.

For the examination, the unsaponifiable matter is dissolved in the smallest possible quantity of absolute alcohol,[1] and set aside to crystallise. If only very small quantities of colouring matter and resinous substances are present, well-formed crystals are generally obtained; if this is not the case, the unsaponifiable matter is dissolved in 95 per cent. alcohol, and the colouring matter removed by treatment of the hot solution with animal charcoal. The filtrate is then evaporated
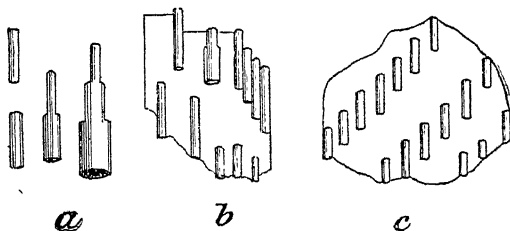
FIG. 39.—Crystals from a mixture of Cholesterol and Phytosterol.

to dryness, the residue taken up with absolute alcohol and allowed to crystallise. The crystals are removed from the mother-liquor and examined under the microscope. If either cholesterol or sitosterol (phytosterol) alone is present, it may frequently be recognised by its characteristic crystalline form, as shown in Figs. 37 and 38. If, however,

[1] A. Bömer, Z. Unters. Nahr. u. Genussm., 1898, 8, 544; J. Soc. Chem. Ind., 1898, 17, 954.

cholesterol and sitosterol are present simultaneously, the microscopic examination yields very uncertain results. A. Bömer showed that mixed crystals are obtained (Fig. 39), whilst in the author's experience the crystallisation of mixtures of cholesterol and sitosterol frequently yields the separate crystals of the two alcohols side by side and not the mixed forms.[1]

The uncertainty of the microscopic method of examination is, however, obviated by the phytosterol acetate test worked out by Bömer.[2] In this test the alcoholic solution containing the crystals which have separated is evaporated to dryness and heated for a short time over a small flame in a dish with 2-3 c.c. of acetic anhydride for each 100 g. of fat, the dish being covered with a watch-glass. The watch-glass is then removed and the excess of acetic anhydride evaporated off on the water-bath. The residue is then heated with the smallest possible quantity of absolute alcohol and set aside to crystallise. To avoid immediate solidification or crystallisation a few cubic centimetres of alcohol are added. The crystallised acetates are collected on a small filter and washed with 95 per cent. alcohol. They are then again placed in the dish, dissolved in 5-10 c.c. of absolute alcohol, and again allowed to crystallise. The crystals are filtered off and their melting point is determined. As cholesterol acetate melts at 114°·3-114°·8 (corr.), whilst the "phytosterols" obtained from various oils and fats gives acetates melting between 125°·6 and 137° (corr.), it is possible to draw a preliminary conclusion as to the presence of cholesterol or phytosterol alone from the melting point of the recrystallised product. In cases of doubt it is advisable to repeat the crystallisation several more times. If the melting point of the fifth crystallisation is still below 116°, the absence of phytosterol may be considered as established.

For the identification of stigmasterol and brassicasterol, and for the detection of traces of paraffin wax with which lard, for instance, may have been adulterated in order to circumvent the phytosterol acetate test, *cf.* J. Lewkowitsch, *Chemical Technology and Analysis of Oils, Fats, and Waxes*, vol. i., pp. 591 *et seq.;* vol. ii., chap. xiv., "Lard."

(b) In Waxes.

As the waxes contain considerable quantities of higher alcohols which prevent a rapid saponification, it is advisable to saponify with $2/N$ alcoholic potash under pressure, or with sodium ethylate. A

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[1] *Cf.* also Lewkowitsch, *Chemical Technology and Analysis of Oils, Fats, and Waxes*, vol. i., p. 584.

[2] *Z. Unters. Nahr. u. Genussm.*, 1901, **4**, 865, 1070; 1902, **5**, 1018; *cf.* also R. H. Kerr, *U.S. Depart. of Agricult. Bureau Animal Chem. Circular* 212, 10th May 1913; *J. Soc. Chem. Ind.*, 1913, **32**, 917.

systematic examination of the unsaponifiable matter from waxes is difficult, and is therefore seldom carried out in commercial analysis.[1]

The melting point of the unsaponifiable matter may furnish a rough guide as to the nature of the substances under investigation. The behaviour towards acetic anhydride permits of definite conclusions as to the alcoholic or hydrocarbon nature of the substance, and in certain cases, such as spermaceti, for the identification of the wax. For this purpose the mixture of unsaponifiable substances is boiled with double its quantity of acetic anhydride for a short time under a reflux condenser. The appearance of the hot solution is then observed. If all has passed into solution, aliphatic alcohols or cholesterol and "phytosterol" are present and have undergone acetylation. If, on the other hand, an undissolved oil floats on the surface of the hot acetic anhydride solution, paraffin wax or ceresin is present. The aliphatic alcohols generally remain dissolved in the acetic anhydride even after cooling. If a mass of crystals separates out, it may be concluded that cholesterol or "phytosterol" is present, although the presence of higher aliphatic alcohols is not excluded.

A summary of those characteristics which will prove of assistance in the examination of the solid unsaponifiable substances is given in the subjoined Table (p. 143).

2. The Detection and Determination of Admixed Unsaponifiable Substances.

The presence of admixed unsaponifiable substances in oils and fats is generally indicated by abnormally low saponification values. Solid unsaponifiable substances such as paraffin wax and ceresin are identified, in absence of waxes, by their state of aggregation and melting point. As a rule, especially in liquid fats, any admixed unsaponifiable matter consists of liquid substances belonging to one of the three following groups :—

(a) Mineral oils.

(b) Rosin oils.

(c) Tar oils.

The three classes of oils are scarcely ever present simultaneously. It is therefore only necessary to consider the possible presence of mineral oil together with rosin oil, or of rosin oil together with tar oil.

It should be observed that a certain percentage of mineral oil is not necessarily to be considered as an adulteration, as it often happens (as for instance in burning oils or lubricating oils) that mineral oil is legitimately added to fatty oils. To ascertain more closely the nature

[1] For further details, cf. Lewkowitsch, *Chemical Technology and Analysis of Oils, Fats, and Waxes*, vol. i., chap. ix.

Table 24.

Some Unsaponifiable Substances and their Characteristics.

	Formula.	Melting point.	Iodine absorption.	Acetates. Saponification value.	Acetates. Melting point.	Increase of weight on boiling with acetic anhydride.*
		°C			°C.	Per cent.
Parafﬁn wax, ceresin	...	88 to 82	3·9 to 4·0†	...	...	0
Cetyl alcohol	$C_{16}H_{34}O$	50	0	197·5	22 to 23	17·2
Octodecyl alcohol	$C_{18}H_{38}()$	59	0	180·0	31	15·5
Ceryl alcohol	$C_{26}H_{54}O$	79	0	132·3	65	11·0
Melissyl (myricyl) alcohol	$C_{30}H_{62}O$	85	0	116·7	70	9·6
Cholesterol	$C_{27}H_{46}O$	148·5	65·8‡	131·1	114	10·9
Isocholesterol	$C_{27}H_{46}O$	137 to 138	(65·8)	131·1	under 100	10·9
Phytosterol, sitosterol	$C_{27}H_{46}O$	137 „ 138	(65·8)	131·1	125·6 to 137	10·9
Stigmasterol	$C_{20}H_{48}O$	170	119·8**	120·4	141	9·9
Alcohols from sperm oil	?	25·5 to 27·5	64·6 to 65·8§	161 to 190	...	...
„ carnauba wax	?	88 „ 90	...	104·9	...	10·2
„ wool wax	?	44·4 „ 48·9	36	136·2	...	10·84
„ crude wool wax	?	...	...	150·6¶	...	...
beeswax	?	75 to 76; 65 to 66·1	...	99 to 103; 94 to 102	...	6·5 to 7·7; 3·8 to 4·1
Hydrocarbons from beeswax	?	49·5 to 59·2	20 to 22	...	...	...
Alcohols from spermaceti	?	46·7	...	184·9	...	15·64
„ insect wax	?	78	...	123·5	...	8·12 to 8·87

* Lewkowitsch, J. Soc. Chem. Ind., 1896, 15, 14.   † Determined in the author's laboratory.

‡ The author found 67 to 68, using Hübl's solution of iodine   Wijs's solution gave unreliable results, ranging up to more than 145.

§ The iodine values of the fractions into which the mixture of alcohols was separated were found to be as follows: (1) 46·48; (2) 63·3; (3) 69 8; (4) 81·8; (5) 84·9 (J. Soc. Chem. Ind., 1892, 11, 185).

¶ Iodine value, 44·08.

** Calculated by the author on the assumption that 4 atoms of iodine are taken up, since stigmasterol gives a well-defined tetrabromide.

of the isolated unsaponifiable oil, a quantity sufficient for the examination is prepared, and the specific gravity is first determined. As the mineral oils in question have a sp. gr. of 0·84-0·92, and the rosin oils 0·96-1·01, whilst the tar oils have a gravity over 1·01, the specific gravity may give useful indications, if only one oil is present. If a mixture of mineral oil and rosin oil is present, the Liebermann-Storch reaction is the best test for the qualitative detection of rosin oil. In this test, 1-2 c.c. of the unsaponifiable oil are gently warmed with acetic anhydride in a test tube and shaken. After cooling, the bottom layer is removed by means of a finely drawn out pipette, and the solution tested as described above (p. 130). In presence of rosin oil a beautiful violet fugitive colour is obtained. It must not be forgotten that cholesterol gives a similar colour reaction. The presence of rosin oil may also be ascertained by the determination of the optical rotation, as mineral oils rotate the plane of polarised light but little, whereas rosin oils show a marked optical activity. (It must not, however, be overlooked that the hydrocarbons obtained from the distillation of wool fat are also optically active, as first shown by the author.)

The quantitative determination of rosin oil in mineral oil is best effected by Valenta's method :—10 c.c. of glacial acetic acid dissolve at 50°, 0·2833-0·6849 g. or 2·6-6·5 per cent. of mineral oil as compared with 1·7788 g. or 16·9 per cent. of rosin oil. For the determination, 2 c.c. of the unsaponifiable oil are mixed with 10 c.c. of glacial acetic acid in a test tube, which is then loosely corked and heated for five minutes in a water-bath with frequent shaking. The solution is then filtered through a moistened filter paper, and the middle portion of the filtrate collected. A weighed quantity of this is titrated to determine the acetic acid. The difference between the percentage of acid found and that originally taken gives the quantity of undissolved oil.[1]

If the sample consists of a mixture of mineral oil and tar oil, the presence of the latter is detected by treatment with nitric acid of sp. gr. 1·45. Tar oils cause a considerable rise of temperature, whereas mineral oils become only slightly warmer.

For details of Valenta's proposal to treat the unsaponifiable oils with dimethyl sulphate, *cf.* J. Lewkowitsch, *Chemical Technology and Analysis of Oils, Fats, and Waxes*, vol. i., p. 611.

With the aid of the subjoined Tables 25-27, which are arranged as far as feasible according to a natural system, it will not be difficult to identify a sample of oil, fat, or wax, when the above described methods have been applied. More complete Tables are given in the author's *Laboratory Companion to Fats and Oils Industries.* A series of examples

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[1] *Cf.* Lewkowitsch, *Chemical Technology and Analysis of Oils, Fats, and Waxes,* vol. iii., chap. xv.

which may serve as a guide to the investigation of more complex problems, are given in vol i., chap. xi., of the author's *Chemical Technology and Analysis of Oils, Fats, and Waxes.* The special methods described in the following Section should also be consulted.

LITERATURE.

LEWKOWITSCH, J.—*Chemical Technology and Analysis of Oils, Fats, and Waxes,* Vol. I., 5th edition, 1913 ; Vols. II. and III., 4th edition, 1909.
LEWKOWITSCH, J.—*The Laboratory Companion to Fats and Oils Industries,* 1901.

Table 25.—Data for the Identification

OILS.	Sp. gr. °C.	Sp. gr.	Solidifying point. °C.	Melting point. °C.	Saponification value. KOH. mg.	Iodine value. Per cent.	Reichert (R.) or Reichert-Meissl (R.-M.) value. N/10 KOH. c.c.	Insoluble fatty acids + unsaponifiable matter. Per cent.
								Vegetable
DRYING.								
Linseed	15	0·9315-0·9345	−27	−20	192-195	171-201	...	95·5
Tung oil, Chinese (Japanese) wood*	15	0·9360-0·9432	below −17	...	193	150-165	...	92·2
Candle nut	15·5	0·9256	...	liq. at −18	192·6	163·7	...	95·5
Hemp seed	15	0·9255-0·9280	−27	...	192·5	148	...	...
Walnut	15	0·9250-0·9260	−27·5	...	195	145	...	95·4
Safflower	15·5	0·9251-0·9280	...	...	186·6-193·3	129·8-149·9	1·54 (R.-M.)	95·37
Poppy seed	15	0·9240-0·9270	−18	...	195	133-143	0	95·2
Sunflower	15	0·9240-0·9258	−18·5	...	193·5	119-135	...	95
SEMI-DRYING.								
Cotton seed group—								
Soja bean	15	0·9242-0·9270	−8	...	192·7	137-140	...	95·5
Cameline (German Sesamé)	15	0·9200-0·9260	−18	...	188	135-142	...	...
Pumpkin seed	15	0·9237	−15·5	...	188·4	123-130	...	96·2
Maize	15·5	0·9213-0·9255	−10 to −20	...	188-193	113-125	4-5 (R.-M.)	93-96
Kapok	18	0·9199	...	...	181	116	...	94·9
Cotton seed	15	0·9220-0·9250	...	3-4	193-195	108-110	...	95-96
Sesamé	15	0·9230-0·9237	−5	...	189-193	103-108	1·2 (R.-M.)	95·7
Beech nut	15	0·9200-0·9225	−17	...	191-196	104-111	...	95·2
Brazil nut	15	0·9180-0·9185	0-4	...	193·4	106·2	...	...
Curcas	15·5	0·9204	−8	...	193·2	98-110	0·5 (R.-M.)	95·3
Croton	15	0·9500	−16	...	210-215	102-104	12-13·6 (R.-M.)	89·0
*Rape group—*Ravison	15·5	0·9183-0·9217	−8	...	174-179	101-122	...	...
Hedge mustard	15	0·9175	−8	...	174	105	...	...
Rape (Colza)	15·5	0·9132-0·9168	−2 to −10	...	170-179	94-102	0·3	95·1
Black mustard seed	15	0·916-0·920	−17	...	174	96-110	...	95·1
White mustard seed	15·5	0·914-0·916	−8 to −16	...	170-174	92-97	...	96·2
Radish seed	15	0·9175	−10 to −17·5	...	173-178	93-96	0·33 (R.-M.)	95·9
Jamba	15	0·9154	−10 to −12	...	172·3	95·4	...	...
NON-DRYING.								
Almond group—								
Cherry kernel	15	0·9234	−19 to −20	...	193-195	110-114	...	...
Apricot kernel	15·5	0·9195	−14	...	192·5	96-108	0	95·4
Plum kernel	15	0·9160-0·9195	−5 to −6	...	191·5	93·3-100·3	...	...
Peach kernel	15	0·918-0·9215	below −20	...	192·5	93-109	...	...
Almond	15	0·9175-0·9195	−10 to −20	...	191	93-97	...	96·2

of Vegetable Oils and of Animal Oils.

		Variables.				Characteristics of fatty acids.									
Refractive index. Butyro-refractometer.		Acetyl value.	Acetyl value.	Acid value.	Unsaponifiable matter.	Sp. gr.		Solidifying point.		Melting point.	Neutralisation value.	Iodine value.		Refractive index.	
°C.	Scale divisions.			KOH. mg.	Per cent.	°C.		°C.	Titre. °C.	°C.	KOH. mg.	Total fatty acids.	Liquid fatty acids.	°C	

Oils.

°C.	Scale divisions.	Acetyl value.	Acetyl value.	Acid value KOH. mg.	Unsap. Per cent.	Sp. gr. °C.	Sp. gr.	Solid. °C.	Titre. °C.	Melt. °C.	Neutr. KOH. mg.	Total fatty acids.	Liquid fatty acids.	°C	Refr. idx.
20	84-90	...	3·98	0·8-8·4	0·42-1·1	15·5	0·9233	13-17	19·4 to	17-21	197	179-182	190-201	60	1·4546
40	72·5	...							20·6						
...	...	...		7·6-12	0·44	...	...	31; 34	37·2	31;	188·8	144-159	...	...	...
										43·8					
15	76	...	9·86	8·1	0·76	...	...	13	...	20-21	...	...	...	...	...
...	...	...		...	1·08	...	...	15	16·6	18-19	...	141	...	...	...
40	64·8	...		...	...	...	...	16	...	16-18	...	150	167	...	...
40	65·2	...	16·1	0·33-20	...	...	...	...	...	...	...	...	...	...	...
40	63·4	...		0·7-11	0·43	100	0·8886	16·5	16·2	20·5	199	139	150	60	1·4506
25	72·2	...		11·2	0·31	...	...	18	...	22-24	201·6	124-134	154·3	60	1·4531
..	...	...		4·5	0·22	...	...	24	...	28	...	119	...	...	...
...	...	...		...	...	...	...	14-13	...	18-20	...	136·8	165·4	...	...
25	70·2-72·5	...		...	...	...	...	24·5	...	28-29	197	...	...	...	...
...	...	...	7·5 to 8·75	1·7-20·6	1·35-2·86	...	...	16-14	...	18-20	198·4	119·5	140-144	...	...
...	...	...		...	...	...	0·9162	24-23	...	29	191	108	...	...	...
25	67·6-69·4	...	7·6 to 18	0	0·78-1·64	15·5	0·9206 to 0·9219	32-35	32-35	35-38	202-208	111-115	147-151	60	1·4460
25	68	...		0·23 to 66 (!)	0·95-1·32	...	...	23·5	22·9 to 23·8	26-32	200·4	110·45	129-136	60	1·4461
...	...	...		...	...	...	...	17	...	23-24	...	114	...	...	...
...	...	...		...	...	...	...	32-25	...	29	...	108	...	...	...
25	65	...	7·5	0·7-8·5	0·5-0·58	...	...	26·5 to	28	27·5 to	...	105·1	...	..	...
40	56·5	...						25·7		30·5					
27	77·5	...	19-32	...	0·55	...	...	16·7	19	...	201	111·5	...	...	...
20	73-74	...		4·8-12	1·45-1·66	100	0·8802	...	...	...	...	...	124·2	...	...
25	70·5-71·5	...		...	...	...	...	...	...	...	...	...	...	...	...
25	68	...	14·7	1·4-13·2	0·58-1	100	0·8758	16	12-13	16-19	185	99-103	121-125	60	1·4991
40	59·5	...		1·36 to 7·35	...	...	...	15·5	...	16	...	109·6	...	...	...
40	58·5	...		5·4	...	...	...	...	...	15-16	...	95·3	...	...	...
40	57·5	...		14·5	...	...	...	15-13	...	20	...	97·1	...	...	...
...	...	...		...	...	...	...	16-11	...	19-21	173·9	96·1	...	...	...
...	...	..		...	...	...	...	15-13	...	19-21	189	109	124·7	...	...
25	66·6	...		0·64	...	...	...	0	...	3·4	194	103	111·5	...	...
...	...	...		0·55	...	...	...	15-13	...	20-22 3·5	200·5	103 (!)	98·6	...	...
25	66·1-67·2	...		...	...	...	...	...	13 to 13·5	10-18	200·9	94-101	101·9	...	...
25	64·4	...		1·5	...	...	...	5	10·1 to 11·8	13-14	204	93-96·5	101·7	60	1·4461

Table

OILS.	Sp. gr. °C.	Sp. gr.	Solidifying point. °C.	Melting point. °C.	Saponification value. KOH. mg.	Iodine value. Per cent.	Reichert (R.) or Reichert-Meissl (R.-M.) value. N/10 KOH. c.c.	Insoluble fatty acids+unsaponifiable matter. Per cent.
Vegetable								
NON-DRYING (*cont.*).								
Olive group—Arachis (earth nut)	15	0·9170-0·9209	– 3 to 0	0	190-196	83-100	...	95·8
Hazel nut	15	0·9146-0·9170	– 17	...	192	83-90	0·99 (R.-M)	95·6
Olive	15	0·916-0·918	– 6 to 2	...	185-196	79-88	0·3	95
Olive kernel	15	0·9184-0·9191	...	...	183	87·4	...	...
Ben	15	0·9120-0·9198	0	...	...	82	...	...
Castor group—								
Grape seed	15	0·935	– 10 to – 13	...	178·5	96	0·46 (R.-M.)	92·13
Castor	15·5	0·9600-0·9679	– 10 to – 18	...	183-186	83-86	1·4	...
Animal								
MARINE ANIMALS.								
Fish—Menhaden	15·5	0·927-0·933	– 4	...	190·6	139-173	1·2	...
Sardine	15	0·9330	...	...	...	161-193	...	94·5
Japanese sardine (Japanese fish oil)	15	0·9160	...	20 to 22	189·8-192·1	100-164	...	96-97
Herring	15·5	0·9202-0·939	...	...	171-194	123·5-142	...	95·64
Stickleback	...	...	...	...	...	162·0	...	95·78
Sturgeon	15	0·9236	...	...	186·3	125·3	...	...
Sprat	15·5	0·9284	...	...	...	...	...	...
Liver—Cod	15	0·9210-0·9270	0 to – 10	...	171·0-189	167	...	95·3
Haddock	15	0·9298	...	...	188·8	154·2	...	93·3
Skate	15	0·9307	...	...	185·4	157·3	...	94·7
Tunny	...	...	...	...	...	155·9	...	95·79
Shark (Arctic)	15	0·9163	...	...	161·0	114·6	...	86·9
Coal fish	15	0·925	...	...	177-181	137-162	...	...
Hake	15·5	0·9270	...	...	...	...	...	...
Ray	15·5	0·9280	...	...	...	...	...	...
Ling	15	0·9200	...	...	184·1	132·6	...	...
Blubber—Seal	15	0·9155-0·9263	– 2 to – 3	...	189-196	127-141	0·07-0·22	95·45
Whale	15·5	0·9250	below – 2	...	188·0	121-136	0·7-2·04	93·5
Dolphin (body)	15	0·9180	below – 3	...	197·3	99·5	5·6	93·07
Dolphin (jaw)	...	...	...	...	290	32·8	65·92	66·28
Porpoise (body)	15	0·9258	– 16	...	195	...	23·5	...
Porpoise (jaw)	15	0·9258	...	...	254-272	22-50	47·77-65·8	70·23
LAND ANIMALS.								
Sheep's foot	15	0·9175	0 to – 15	...	194·7	74·2	...	...
Horse's foot	15	0·918-0·927	...	...	195·9	73·8-90	...	...
Neat's foot	15	0·914-0·916	0 to – 15	...	194·3	69·3-70·4	...	...
Egg	15	0·9144	8 to – 10	22·25	184·4-190·2	68·5-81·6	0·4-0·7	95·16

25—*continued.*

	Variables.							Characteristics of fatty acids.							
Refractive index.		Acetyl value.	Acetyl value.	Acid value.	Unsaponifiable matter.	Sp. gr.		Solidifying point.		Melting point.	Neutralisation value.	Iodine value.		Refractive index.	
Butyro-refractometer.															
°C.	Scale divisions.			KOH. mg.	Per cent.	°C.		°C.	Titre. °C.	°C.	KOH. mg.	Total fatty acids.	Liquid fatty acids.	°C	
Oils—*continued.*															
25	66-67.5	...	...	1.2 to 32 (!)	0.54-0.94	100	0.8790	26	29.2	27 7 to 32	201.6	96-103	105-128	60	1.4461
...	...	...	3.2	...	0.5	...	...	19-20	...	22-24	200.6	90.3	91.3 to 97.6	...	...
25	62.4	...	10.64	1.9-50	0.46-1	100	0.8749	22-17	17.2 to 26.4	24-27	193	86-90	95.5 to 103.5	60	1.4410
...	...	...	...	2-3.5	...	...	...	...	...	...	...	...	...	...	...
...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...
25	78	146.7 to 150	...	16.2 / 0.14 to 14.61	...	15.5	0.9509	20-18 / 3	...	24 / 13	187.4 / 192.1	99 / 87-93	106.9	60	1.4546
Oils.															
...	...	...	...	11.6	1.6-2.2	...	...	...	...	...	...	...	...	...	...
...	...	...	...	4-21	0.52-0.86	...	...	...	...	...	...	...	...	...	...
...	...	...	13.0	10-35	0.48-2.6	...	...	...	28.2	...	...	...	...	...	...
...	...	...	...	1.8-44	0.99-10.7	...	...	...	...	...	178.5	...	...	...	...
...	...	...	...	21	1.73	...	...	...	...	...	181.5	...	...	...	...
...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...
25	75	...	4-8	1-25	0.54-7.83	...	...	...	18.4 to 24.3	21-25	204-207	130.5 to 170	...	60	1.4521
...	...	...	...	...	1.1	...	...	...	...	...	...	...	...	...	...
...	...	...	10.6	...	0.97	...	...	...	...	...	...	...	...	...	...
...	...	...	...	0.2-34	1.0-1.8	...	...	...	...	...	177.0	...	...	...	...
...	...	...	11.9	...	10.2	...	...	...	...	...	...	...	...	...	...
...	...	...	...	1.26 to 1.68	...	...	...	...	...	...	...	...	...	...	...
..	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...
...	...	...	...	11.0	2.23	...	...	...	...	...	...	...	...	...	...
...	...	...	16.5	1.9-40	0.38-1.4	...	...	...	15.5 to 15.9	22-23	193.2	...	...	...	...
25	70	...	...	0.5-37	0.92-3.72	100	0.8922	...	23.9	27.0	...	131.2	144.7	...	...
...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...
...	...	...	...	...	3.7	...	...	...	...	...	...	...	...	...	...
...	...	...	...	5.0	16.4	...	...	...	...	...	...	...	...	...	...
...	...	...	...	...	...	...	...	...	21.1 / 2.86	...	...	...	...	...	...
...	...	...	13.0	...	...	...	...	...	...	...	...	...	...	...	...
...	...	...	22.0	...	...	...	...	...	26.1 to 26.5	29.8 to 30.8	...	61.98 to 63.26	...	...	...
25	68.5	...	...	1.2	1.7	...	...	...	34-39	...	194.9	72.9	...	...	...

Table 26.—Data for the Identification

FATS.	Sp. gr. °C.		Solidifying point. °C.	Melting point. °C.	Saponification value. KOH. mg.	Iodine value. Per cent.	Reichert (R.) or Reichert-Meissl (R.-M.) value. N/10 KOH. c.c.	Insoluble fatty acids + unsaponifiable matter. Per cent.
VEGETABLE.								
Laurel oil group—								
Laurel oil	15	0·9332	25	32-34	197·9	68-80	1·6	...
Mahua butter	100 (100=1)	0·8981	19-22	28-31	190-194	53-67	0·5-0·9 (R.-M.)	94·82
Mowrah seed oil	15	0·9175	36	42	188-192	50-62	...	94·76
Macassar oil	15	0·9240	10	22	221·5	48-55	...	91·5
Shea butter (Galam butter).	15	0·9175	17-18	25·3	179-192	56·6	...	94·76
Palm oil	15	0·921-0·9245	...	27-42·5	196-202	51·5	0·5	94·97
Nutmeg butter	15	0·945-0·996	41-42	38-51	154-191	40-52 (50-81)	1-4·2 (R.-M.)	...
Cocoa group—Mkányi	15	0·9298	38	40-41	190·5	41·9	1·21 (R.-M.)	95·65
Malabar tallow	15	0·9150	30·5	36·5	188·7-192	38·2	...	0·2 to 0·44 (R.-M.)
Cocoa butter	15	0·9500-0·976	23-21·5	28-33	193·55	32-41	0·2-0·8 (R.-M.)	94·59
Chinese vegetable tallow	15	0·9180	27-31	36-46	200·3	28-37	...	...
Kokum butter (Goa butter).	40 (15=1)	0·8952	37·6 to 37·9	41-42	187-191	33·6	0·1-1·5 (R.-M.)	95·1
Borneo tallow	...	...	...	35-42	...	(31 ?)	...	...
Cocoa nut oil group—								
Mocaya oil	...	...	22	24-29	240·6	24·63	7·0 (R.-M.)	...
Maripa	100 (15·5=1)	0·8686	24-25	26·5 to 27·0	270·5	17·35	4·45 (R.-M.)	88·88
Palm seed oil	15 (15·5=1)	0·9520	20·5	23-28	242-250	13-14	5-6 (R.-M.)	87·6 to 91·1
Cocoa nut oil	40 (15·5=1)	0·9115	22-14	21-24	246-260	8-9·5	7-8·4 (R.-M.)	88·6-90
Myrtle wax	15	0·995	39-43	40-44	208·7	10·7	...	...
Japan wax	15	0·9700-0·980	48·5-53	50-54	217-237·5	4·9-8·5	...	90·6
Dika oil (oba oil, wild mango oil)	...	0·8200	34·8	41·6	...	31·1	...	...
ANIMAL.								
Drying—Polar bear	15	0·9256	...	...	187·9	147	...	...
Semi-drying—								
Black cock	15	0·9296	...	...	201·6	121·1	2·1	...
Hare	15	0·9349	17-23	35-40	200·9	102·2	1·59	95·4
Rabbit (wild)	15	0·9393	17-22	35-38	199·3	99·8	0·7	...
,, (tame)	15	0·9342	22-24	40-42	202·6	67·6	2·8	95·5
Wild duck	...	...	15-20	...	198·5	84·6	1·3	...
Tame duck	...	...	22-24	36-39	58·5	...	...	...
Horse	15	0·9189	43-30	34-54	195-197	71-86	0·2-0·4	95-96

of Vegetable and Animal Fats.

	Variables.					Characteristics of fatty acids.							
Refractive index.		Acetyl value.	Acid value.	Unsaponifiable matter.	Sp. gr.		Solidifying point.		Melting point.	Neutralisation value.	Iodine value.		Refractive index.
Butyro-refracto-meter.													
°C	Scale divisions.		KOH. mg.	Per cent.	°C.		°C.	Titre. °C.	°C.	KOH. mg.	Total fatty acids.	Liquid fatty acids.	°C.
..	...	...	26·3	...	...	...	...	15·1	...	...	81·8	...	...	...
40	52·1	...	...	...	...	...	...	..·	...	...	...	...	...	...
...	...	...	34·56	...	...	...	38-40	40·3	45	...	56·6	...	...	...
...	...	...	6·2 to 35·4	3·12	...	...	...	51·6 to 53·2	52-55	191·6	50-58	103·2	...	...
...	...	...	29·4	3·5	...	...	38	53·8	58	...	56-57·2	...	...	...
...	...	18	24-200	...	100	0·8701	...	35·9 to 45·5	47-50	205·6	53·3	92·6	...	...
40	48-85	...	17-44·8	...	...	...	40	35·9	42·5	...	...	...	...	...
...	...	...	23·3	...	...	...	57·5	61·5	59 to 61·5	...	42·1	...	...	...
...	...	...	38	...	...	...	54·8	...	56·6	...	...	...	...	...
40	46-47·8	2·8	1·1 to 1·88	...	...	...	47-45	48·3	48-50	190	33-39	...	60	1·422
...	...	...	2·2-7·5	...	...	...	...	45·2 to 53·5	53-57	182-208	30-39	...	...	...
25	1·4628	...	21	...	...	...	59·4	...	60-61	198·9	...	...	...	...
...	...	...	20	...	...	...	53·5 to 54	...	...	...	...	...	...	...
...	...	...	...	...	...	...	22-20	...	23-25	254	...	...	...	...
...	...	...	...	...	100 (15·5=1)	0·8230	25	...	27·5 to 28·5	...	12·15	...	...	...
40	36·5	1·9 to 8·4	8·36	...	...	...	...	20·5 to 25·5	25 to 28·5	258-264	12·0	...	60	1·4310
40	+34	0·9 to 12·3	5-50	...	98-99 (15·5=1)	0·8354	20-16	22·5 to 25·2	25-27	258-266	8·4-9·3	18·6	60	1·4295
...	...	27 to 31·2	3-4·4 7·33	1·1 to 1·63	98-99 (15·5=1)	0·8480	46 53·0 to 56·5	...	47·5 59·4	230·9 56-62 213·7	...	...	...	...
...	...	...	19·6	...	...	...	...	...	...	...	...	...	...	...
...	...	...	...	...	...	...	...	...	...	...	...	...	...	...
...	...	...	5·9	...	15	0·9374	25-28	...	30-33	199·3	120	...	...	...
40	49	...	2·73	...	15	0·9361	36-40	...	44-47	209	93·3	...	40	But'r. refr. 36
...	...	...	7·2	...	15	0·9246	35-36	...	39-41	209·5	101·1	...	...	...
40	49	...	6·2	...	15	0·9264	37-39	...	40-42	218·1	64·4	...	40	But'r. refr. 36
...	...	...	1·5	...	...	...	30-31	...	36-40	...	...	...	...	...
...	...	...	...	...	...	...	...	...	...	...	...	...	...	...
40	53·7	...	0-2·44	...	...	...	37·7	33·7	37·5 to 39·5	202·6	84-87	...	...	...

Table

FATS.		Sp. gr.		Solidifying point.	Melting point.	Saponification value.	Iodine value.	Reichert (R.) or Reichert-Meissl (R.-M.) value.	Insoluble fatty acids + unsaponifiable matter.
		°C.		°C.	°C.	KOH. mg.	Per cent.	N/10 KOH. c c.	Per cent.
ANIMAL (*cont.*).									
Non-drying—									
Horse marrow . .		15	0·9204-0·9221	24-20	35-39	199·8	79·1	1	...
Goose (domestic) .		15	0·9274	18-20	32-34	193·1	67-71	0·98	95
Wild goose . .		15	0·9158	18-20	...	196	99·6	0·2-0·3 (R.-M.)	...
Lard . . .		15	0·934-0·938	27·1 to 29·9	36-40·5	195·4	50-70	...	93-96
Wild boar . .		15	0·9424	22-23	40-44	195·1	76·6	0·68	...
Beef marrow . .		15	0·9311-0·9380	31-29	37-45	199	55·4	1·1	...
Bone . . .		15	0·914-0·916	15-17	21-22	190·9	46-55·8	...	...
Beef tallow . .		15	0·943-0·952	35-27	45-40	193·2-200	38-46	0·25	95·6
Mutton tallow . .		15	0·937-0·953	36-41	44-45	192-195·2	35-46	...	95·5
Butter . . .		15	0·926-0·940	20-23	28-33	227	26-38	12·5-15·2	86·5 to 89·8
Stag . . .		15	0·9670	39-48	49-52	199·9	20·5-25·7	1·66	...

Table 27.—Data for the

WAXES.		Sp. gr.		Solidifying point.	Melting point.	Saponification value.	Iodine value.	Reichert (R.) or Reichert-Meissl (R.-M.) value.
		°C.		°C.	°C.	KOH. mg.	Per cent.	N/10 KOH. c.c.
Liquid—								
Sperm oil . .		15	0·8799-0·8835	...	...	125·2-132·6	81-90	1·3
Bottlenose oil .		15	0·8764	...	...	123-135·9	67-82·1	1·4
Vegetable—								
Carnauba . .		15	0·990-0·999	80-81	85-86	79-95	13·5	...
Animal—								
Wool (wool fat) .		17	0·9413-0·9449	30-30·2	31-35	102·4	17·1-28·9	...
Bees . . .		15	0·964-0·970	60·5-62·8	61·5-64·4	90-98	7·9-11	0·34-0·54
Spermaceti . .		15	0·905-0·960	42-47	42-49	123-135	...	...
Insect (Chinese) .		15	0·926-0·970	80·5-81	80·5-83	80·5-93	...	...

26—continued.

°C.	Scale divisions.	Acetyl value.	Acid value. KOH. mg.	Unsaponifiable matter. Per cent.	Sp. gr. °C.	Sp. gr.	Solidifying point. °C.	Solidifying point. Titre. °C.	Melting point. °C.	Neutralisation value. KOH. mg.	Iodine value Total fatty acids.	Iodine value Liquid fatty acids.	°C	Refractive index.
...	...	...	1	...	15	0·9182 to 0·9289	36-34	...	42-44	210·8 to 217·6	71·8 to 72·2	...	...	...
40	50-50·5	...	0·59	...	15	0·9257	31-32	...	38-40	202·4	65·3	...	..	...
...	...	...	0·86	...	15	0·9251	33-34	...	34-40	196·4	65·1	...	...	...
40	48·6 to 51·2	2·6	0·54 to 1·28	0·23	99	0·8445	39	41-42	43-44	201·8	64	92·1* / 90-106†	60 / 22	1·4395 Oil refr. − 30
..	...	...	2·6	...	15	0·9333	32·5 to 33·5	...	39-40	203·6	81·2	...	...	...
...	...	4·2	1·6	...	15	0·9300 to 0·9399	37·9 to 38	...	44-46	204·5	55·5	...	...	...
...	...	11·3	29·6-53	0·5 to 1·8	...	...	28	...	30	200	55·7 to 57·4	...	...	...
40	49	2·7 to 8·6	3·5-50	...	100 (100=1)	0·8698	...	37·9 to 46·2	43-44	197·2	41·3	92·4	60	1·4375
...	...	...	1·7-14	...	...	...	41	40·15 to 48·2	49-50	210	34·8	92·7	60	1·4374
40	41-42	1·9 to 8·6	0·45 to 35·38	...	37·75 (15·5=1)	0·9075	33-38	...	38-40	210-220	28-31	...	60	1·437
40	44·5	...	3·5	...	15	0·9685	46-48	...	50-52	201·3	23·6	...	...	...

* European lard.   † American lard.

Identification of Waxes.

°C.	Scale divisions.	Acetyl value.	Acid value. KOH. mg.	Fatty acids Per cent.	Sp. gr. °C.	Sp. gr.	Solidifying point. °C.	Solidifying point. Titre. °C.	Melting point. °C.	Mean molecular weight.	Iodine value. Per cent.
40	46·2	4·5-6·4	...	60-64	15·5	0·899	16·1	11·1-11·9	13·3	281-294	83·2-85·6
...	...	4·1-6·4	...	61-65	...	...	10	8·3-8·6	10·3-10·8	...	82·7
...	...	55·24	4-7	...	..	...	...	...	...	...	...
...	...	23·3	...	59·8	...	...	40	...	41·8	327·5	17
62	29·5-30	15·24	16·8-21·2	...	...	...	...	...	...	...	...
...	...	2·63	...	...	...	...	...	...	...	...	...
...	...	...	...	...	...	...	...	...	...	...	...

SPECIAL METHODS OF ANALYSIS EMPLOYED IN THE OIL AND FAT INDUSTRIES

By the late J. LEWKOWITSCH, M.A., Ph.D. English translation
revised by the Author.

A.—OIL SEED, OIL CAKES, CRUDE FATS, ETC.

THE raw materials of the oil and fat industries in which the content of fat is to be determined are subdivided as finely as possible, and extracted with ether, petroleum spirit, or other such solvents. The disintegration of the hard oil seeds may be effected by pounding in a porcelain mortar; in this case, it is necessary to rinse out the mortar with the solvent to avoid losing any fat which has been pressed out. Oil seeds may also be ground in an ordinary coffee mill, but in this case it is impossible to avoid loss of oil. M. Lehmann[1] has constructed a
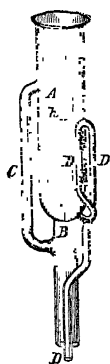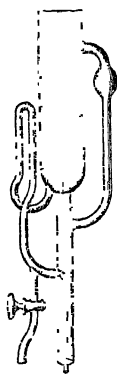
grinding mill of such small dimensions that after grinding the sample the whole mill may be put into the extractor, together with the ground material. If the substances contain a considerable amount of moisture, the sample should be dried in an air-oven previously to extraction, provided that this can be done without detriment to the fat; but if any oxidation or loss of volatile ingredients be feared, the complete extraction of moist substances is effected by using petroleum spirit (boiling completely below 80°). Ethyl ether, carbon bisulphide, or chloroform may be used only for dry substances. The choice of solvent is not always immaterial; carbon bisulphide, as a rule, extracts more foreign matter than either ether or petroleum spirit.

FIG. 40.   FIG. 41.

Of the numerous forms of extraction apparatus that have been proposed, that of Soxhlet (Fig. 40) is the most generally employed. A weighed quantity (20-50 g.) of substance is introduced into a "thimble" of filter paper (either bought ready-made or prepared by rolling filter paper round a cylindrical piece of wood). The tube B is then attached to a flask of 100-200 c.c. capacity, and the solvent added at A, until it

[1] *Chem. Zeit.,* 1894, **18**, 412.

overflows the syphon.   After adding a little more solvent, A is attached to a reflux condenser and the flask heated on a water-bath.

. In using this form of extractor, it is always a matter of doubt when the extraction is complete, and it is therefore generally carried on longer than is necessary, with consequent loss of time and solvent. For this reason a modified form of Soxhlet's apparatus proposed by the author,[1] and shown in Fig. 41, may be used with advantage; after certain intervals of time a sample is drawn off into a watch-glass, and evaporated down to see if any residue of fat remains.

. When the extraction is complete, the heating is discontinued, the solvent distilled off, and the residue weighed.   As ethyl ether extracts from moist substances not only considerable quantities of water but also non-fatty substances, it is advisable, when using ether, to take up the residual fat with petroleum spirit, after distilling off the ether.

The drying may be done by laying the flask in a drying oven heated to 100°-105°, and turning it round occasionally.   When all droplets of water have disappeared, the drying may be considered complete.   As a check, the substance is dried for another half an hour, and weighed again.   In the case of drying oils, the flask is heated to 100°-105° in an oil-bath, and a slow current of carbon dioxide or hydrogen is passed over the heated fat.   The nature of the extracted fat is determined by the methods described in the foregoing Section on " Oils, Fats, and Waxes."   In the case of oil seeds and oil cakes, a careful microscopic examination gives useful information as to their source, purity, etc.   For further details of this subject, special treatises must be consulted, such as J. König's *Untersuchung landwirtschaftlich und gewerblich wichtiger Stoffe*, pp. 244 and 278.

B.—EDIBLE OILS AND FATS.

The examination of these products is carried out by the methods described in the previous Section.   Most frequently it is required to detect cotton-seed oil, sesamé oil, and arachis oil in table oils, sold under the name of olive oil.   The determination of the acid value is of importance, although it is not always safe to condemn a sample, the acid value of which is somewhat high (over 2), on this test alone.   The taste is rather to be regarded as the determining factor.   This Section is restricted to the examination of the following edible fats :—

I. BUTTER.

The methods of examination to be described are concerned only with butter *fat*.   The butter fat is prepared by melting the sample and pouring off the clear molten fat through a dry pleated filter.

[1] *J. Chem. Soc.*, 1889, 55, 359.

The refractive index serves as a preliminary test (*cf.* p. 109). The determination of the Reichert-Wollny value (p. 119) is of importance, and should exceed 24 in a "normal" butter. If a lower value be obtained, adulteration with other animal fats or vegetable fats may be suspected, except in the case of "abnormal" butters. The former are introduced into butter mostly in the form of margarine. If the margarines contain sesamé oil, prescribed by law in some continental countries, indications of its presence are obtained by a positive result of the Baudouin reaction (p. 129); if this is not the case, the saponification value, specific gravity, etc., and other characteristics (see preceding Section) must be determined,[1] and as margarines contain, as a rule, vegetable fats, the phytosteryl acetate test should be applied.

With the aid of this test the presence of vegetable fats is most rapidly ascertained. The detection of small quantities of cocoa-nut oil in butter fat is of importance. For this purpose E. Polenske's method[2] is the most applicable; in the absence of better methods, this may be regarded as supplementary to the phytosteryl acetate test.
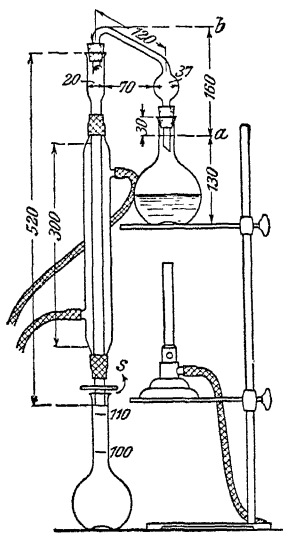
FIG. 42.

To carry out the test, 5 g. of filtered butter fat are saponified by heating in a 300 c.c. flask over a free flame with 20 g. of glycerol and 2 c.c. of a solution of sodium hydroxide in an equal quantity of water (Leffmann and Beam's process). The solution is allowed to cool below 100°, 90 c.c. of water added, and the soap brought into solution by warming on a water-bath to about 50°. The solution should be clear and almost colourless. If a brown solution has been obtained, the test must be rejected. Then 50 c.c. of dilute sulphuric acid (25 c.c. pure concentrated sulphuric acid in 1000 c.c. water) is added to the hot solution, together with some *powdered* pumice. The flask is then attached immediately to a condenser. The apparatus used must correspond precisely in all details with the dimensions given in Fig. 42. The heating must be so regulated that 110 c.c. distil over in nineteen to twenty minutes. The flow of condenser water is regulated so that the distillate is collected in the 110 c.c. flask at a temperature not exceeding 20°-23°. As soon as 110 c.c. have distilled over, the 110 c.c. flask is removed and replaced by a measuring cylinder of 20 c.c. capacity.

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[1] *Cf.* Lewkowitsch, *Chemical Technology and Analysis of Oils, Fats, and Waxes*, vol. ii., p. 667.
[2] *Arbeiten aus. d. Kaiserl. Gesundheitsamt*, 1904, p. 543; *cf.* also R. R. Tatlock and R. T. Thomson, *J. Soc. Chem. Ind.*, 1909, **28**, 69.

The distillate must not be shaken. The flask is immersed almost completely in water at 15°; after about five minutes, the neck of the flask is gently tapped, so that the drops of oil floating on the surface attach themselves to the walls of the flask. After a further lapse of ten minutes, the consistency of the insoluble acids is observed, to see whether they form a solid or semi-solid mass or oily drops. The contents of the flask are then well mixed up, by inverting the closed flask four or five times, without, however, shaking it vigorously. Then 100 c.c. are filtered off through a filter paper of 8 cm. diameter, and titrated with $N/$10 alkali exactly as in the Reichert process (p. 119). In order to remove the soluble acid completely, the filter is washed three times successively with 15 c.c. of water, which have been passed severally through the condenser tube, then into the 20 c.c. measuring cylinder, and finally into the 110 c.c. flask. The condenser tube, measuring cylinder, and 110 c.c. flask are then rinsed out in the same manner with three successive washings of 15 c.c. of neutralised 90 per cent. alcohol, each washing being allowed to drain off completely before the next is brought on to the filter. The alcoholic filtrate is finally titrated with $N/$10 alkali. In the following Table a number of the values published by Polenske for pure butter fats are given, together with the values for the same butter fats containing respectively, 10, 15, and 20 per cent. of cocoa-nut oil. The expression "new butter value" proposed by Polenske has been avoided by the author, as it is better expressed by "titration value of the insoluble volatile acids."

Polenske claimed that with the help of this Table an approximately quantitative estimation of the cocoa-nut oil present in an adulterated butter could be obtained; this is based upon the deduction from the data in the Table, that the amount of alkali necessary for the neutralisation of the insoluble acids is increased by 0·1 c.c. for each per cent. of cocoa-nut oil added. The mode of calculation may be illustrated by an example. Suppose a sample of butter fat gave a Reichert-Meissl value of 24·5 and required 3·0 c.c. of $N/$10 alkali for the neutralisation of the insoluble volatile fatty acids. The insoluble volatile fatty acids were of a liquid consistency. According to the Table a pure butter fat of Reichert-Meissl value 24·5 should require only 1·6 c.c. of $N/$10 alkali for the neutralisation of the insoluble volatile fatty acids; hence 3·0 − 1·6 = 1·4 c.c. was necessary for the neutralisation of the insoluble volatile acids; the sample in question must therefore be considered to have been adulterated with cocoa-nut oil. As each 0·1 c.c. of alkali is taken to correspond to 1 per cent. of cocoa-nut oil, the sample is looked upon as having been adulterated with 14 per cent. of cocoa-nut oil. Examples 15 and 22 of the Table (24·2, 3·0 and 24·8, 3·0) would indicate an addition of 10 per cent. of cocoa-nut oil. The sample which gave the above figures actually contained 10 per cent. of cocoa-nut

oil. A method based upon the same principle, but differing in the practical details, has been described by A. Müntz and H. Coudon.[1]

Table 28.

Titration Values of Butter Fats. (Polenske.)

No.	Titration values, i.e., number of c.c. N/10 KOH required for the neutralisation of the :—							
	Pure butter fat.		Same butter fat with addition of 10 per cent. cocoa-nut oil.		Same butter fat with addition of 15 per cent. cocoa-nut oil.		Same butter fat with addition of 20 per cent. cocoa-nut oil.	
	Soluble volatile acids (Reichert-Meissl value).	Insoluble volatile acids.	Soluble volatile acids (Reichert-Meissl value).	Insoluble volatile acids.	Soluble volatile acids (Reichert-Meissl value).	Insoluble volatile acids.	Soluble volatile acids (Reichert-Meissl value).	Insoluble volatile acids.
1	19·9	1·35	18·7	2·4	18·1	2·9	17·6	3·3
2	21·1	1·4	19·7	2·3	19 2	3·0	18·5	3·6
3	22·5	1·5	21·0	2·5	20·4	2·9	19·8	3·5
4	23·3	1·6	22·0	2·5	21·5	3·1	21·0	3·7
5	23·4	1·5	22·3	2·4	21·7	3·1	21·2	3·7
6	23·6	1·7	22·5	2·5	21·9	3·3	21·4	4·0
7	24·5	1·6	23·3	2·5	22·4	3·1	21·7	3·7
8	24·7	1·7	23·8	2·9	22·9	3·5	22·1	3·9
9	24·8	1·7	23·5	2·7	22·7	3·2	...	...
10	24·8	1·6	23·4	2·5	22·8	3·0	22·1	3·6
11	25·0	1·8	23·0	2·7	23·3	3·1	21·8	3·6
12	25·1	1·6	23·5	2·5	23·1	3·0	22·5	3·8
13	25·2	1·6	23·4	2·6	22·9	3·0	22·3	3·7
14	25·3	1·8	24·0	2·9	23·5	3·5	22·6	4·1
15	25·4	1·9	24·2	3·0	23·7	3·6	22·6	4·1
16	25·6	1·7	24·1	2·7	23·3	3·1	22·7	3·7
17	25·4	1·7	23·8	2·6	23·0	3·1	...	...
18	26·2	1·9	25·0	3·1	24·2	3·6	23·6	4·0
19	26·5	1·9	25·0	2·9	24·1	3·5	23·2	4·1
20	26·6	1·8	25·4	2·9	24·6	3·3	23·9	3·8
21	26·7	2·0	25·2	3·2	24·5	3·6	23·7	4·2
22	26·8	2·0	24·8	3·0	24·2	3·4	23·5	4·0
23	26·9	2·1	25·2	2·9	24·1	3·6	23 2	4·2
24	26·9	1·9	24·9	2·9	24·0	3·3	23·3	4·0
25	27·5	1·9	25·7	2·7	24·9	3·3	24·0	3 9
26	27·8	2·2	26·0	3·1	25·0	3·7	...	...
27	28·2	2·3	26·1	3·1	25·1	3·8	24·5	4·4
28	28·4	2·3	26·5	3·5	25·7	4·0	25·1	4·5
29	28·8	2·2	26·8	3·3	26·0	3·9	...	...
30	28·8	2·5	27·1	3·5	26·3	4·0	25·4	4·7
31	29·4	2·6	27·6	3·8	26·9	4·2	...	...
32	29·6	2·8	27·5	3·8	26·2	4·2	25·5	4·9
33	29·5	2·5	27·4	3·5	26·6	4·1	25·4	4·7
34	30·1	3·0	27·8	3·8	26·9	4·4	26·2	5·0

It must, however, be clearly pointed out that the titration values must not be considered as definite and final indications, as was formerly

[1] *Monit. Scient.* 1904, **18**, 530 ; *J. Soc. Chem. Ind.*, 1904, **23**, 764 ; cf. Lewkowitsch, *Chemical Technology, etc.*, vol. ii., p. 695.

supposed; indeed, as a rule, they do not furnish any more information than the Reichert-Meissl value themselves. For the detection of tallow and hog's lard in butter fat, with the aid of the "difference number" (difference of melting points), *cf.* Lewkowitsch, *Chemical Technology, etc.*, vol. i., p. 324.

2. MARGARINE.

The examination of margarine fat comprises the determination of the Reichert-Wollny value, and in those countries in which sesamé oil must be added, its detection by the Baudouin test. If the quantity of milk prescribed by law in this country (10 per cent. of butter fat) has not been exceeded in the preparation of the margarine, the Reichert-Wollny value must not exceed 4. This is, however, only the case when the margarine contains no cocoa-nut oil, but since the latter has come into use in the manufacture of margarine Reichert's method must, if necessary, be supplemented by Polenske's test. Margarines consisting entirely of cocoa-nut oil are readily identified by the Reichert value, saponification value, iodine value, and titration value of the insoluble volatile acids.

3. LARD, ARTIFICIAL LARD, LARD SUBSTITUTES.

The testing of lard for impurities and the detection of substitutes are among the most important problems in the analysis of edible fats. The refraction is first observed in a (butyro) refractometer; the iodine value of the fat and that of the liquid acids are also determined. If these tests give cause for suspicion, the sample is examined for vegetable oils and fats by the phytosteryl acetate test (p. 141). If cocoa-nut oil or palm kernel oil is suspected, the Reichert-Meissl (Reichert-Wollny) value (p. 119) and the titration value of the insoluble volatile acids (Polenske's method, p. 156) are determined.

The detection of *Tallow* or *Beef Stearine* is a difficult problem; for information the reader is referred to the monograph on "Lard" in the author's *Chemical Technology and Analysis of Oils, Fats, and Waxes*, vol. ii., p. 560.

4. CHOCOLATE FATS, COCOA-BUTTER SUBSTITUTES.

Under the former of these two terms, the author includes all the fats which serve as substitutes for the expensive cocoa-butter in the manufacture of cheap chocolates. These are for the most part "cocoa-nut oil stearine" and "palm kernel stearine," which are recognised by their low iodine values and high saponification values, as also by their Reichert-Meissl values. The melting point of these "stearines" is frequently raised by the addition of tallow or of oleostearine. The determination of the melting point of the fat and the titre test of the fatty acids are of importance.

C.—WOOL OILS.

These are oils which are used to lubricate the wool fibre previous to spinning and weaving. They are either pure fatty oils (olive oil, lard oil, neat's foot oil) or oleic acid, or mixtures of this acid with unsaponifiable oils (mineral oils, wool-fat hydrocarbons).

The value of wool oils depends upon the ease with which they are removed from the fibre by scouring, and further upon their freedom from liability to spontaneous combustion.

The quantitative estimation of the unsaponifiable matter (p. 124) furnishes important information. This is insisted upon by Fire Insurance Companies, as the insurance premium is fixed at a higher rate the greater the amount of unsaponifiable matter present.

The liability to spontaneous combustion is ascertained by determining the flashing point (cf. the sections on " Mineral Oils," p. 28, and " Lubricants," p. 77); and, further, in the case of pure oils and pure fatty acids, by the behaviour of the wool oil to cotton fibre, at a somewhat high temperature in W. Mackey's "Cloth Oil Tester."

This apparatus[1] (Fig. 43) consists essentially of a cylindrical water-bath, closed by a lid in which a thermometer is fixed. In the lid are fitted two tubes A and B, through which air is circulated in the direction of the arrows. The water-bath contains a wire-gauze cylinder C, in which is placed a wad of cotton wool impregnated with the wool oil under examination.
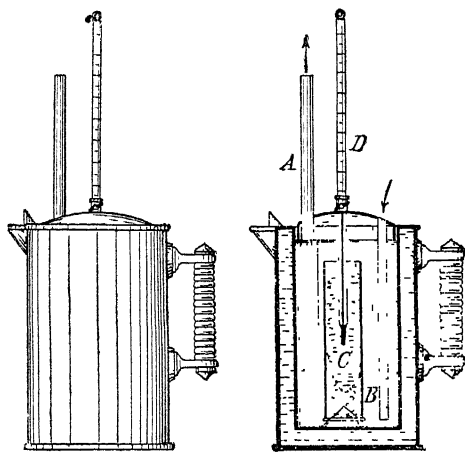
FIG. 43.

To carry out the test, 7 g. of pure cotton wool is weighed out and soaked with 14 g. of wool oil in a flat porcelain dish. This must be done carefully so as to distribute the oil uniformly. It is best to teaze the cotton wool out and to impregnate it carefully with the oil, as the success of the test depends, to a large extent, upon the uniform distribution of the oil. The cotton wool containing the oil is brought into the cylinder C, the thermometer being held firmly so that the cotton wool is packed round the mercury bulb. The water in the steam jacket is heated until it boils vigorously, the cylinder introduced into the bath, the cover brought down over the thermometer and held in place by the clamp D. After about an hour, during which time the

[1] Made by Messrs Reynolds & Branson, Leeds.

water is kept boiling vigorously, the temperature is observed. Moisture must be rigorously excluded.

If, after an hour, the thermometer shows a temperature exceeding 100°, the oil is considered as liable to spontaneous combustion. In the case of very dangerous oils the temperature rises to 200° within forty-five minutes. If the temperature rises above 150° it is advisable to remove the thermometer, as the oiled cotton wool easily becomes ignited.

This method gives only comparative values ; hence the details must be precisely observed. Before proceeding with the experiment, it is advisable to test olive oil and pure cotton-seed oil as examples, representing a safe and a dangerous oil respectively.

D.—LITHOGRAPHIC VARNISHES—POLYMERISED LINSEED OILS.

Lithographic varnishes are obtained by heating drying oils—chiefly linseed oil—to high temperatures in absence of air. The more strongly the oil is heated the more energetic is the resulting polymerisation. The determination of the iodine value does not furnish sufficient data for the valuation of such oils. According to the author,[1] the determination of the yield of insoluble bromides (p. 138) gives reliable results. Thus, whilst raw linseed oil yields up to 42 per cent. of insoluble (hexa) bromides, the yield in the case of highly polymerised oils falls to zero.

The data given in the following Table will serve as a guide in the interpretation of the values found.

Table 29.

Values of Polymerised Linseed Oils—Lithograph Varnishes.
(Lewkowitsch.)

	Sp. gr. at 60° F.	Saponification value.	Iodine value.	Yield of bromides.	Hefner value.	Oxidised fatty acids.	Unsaponifiable matter.	Yield of glycerol.	Acid value.	Acetyl value.	Iodine value of fatty acids.	Liquid fatty acids.
				Per cent.		Per cent.	Per cent.	Per cent.				Per cent.
Raw linseed oil .	0·9308	...	186·4	24·17	...	...	...	...	...	...	...	...
Linseed oil heated to 310° . .	0·9354	...	176·3	8·44	...	...	...	...	...	...	...	...
Thin varnish I. .	0·9676	189·5	107·7	0·17	94·75	4·17	1·76	9·71	6·09	6·5	114·74	39·31
„ II. .	0·9691	193·0	125·3	2·0	94·8	0·34	0·13	...	...	...	...	...
Medium varnish I. .	0·9693	194·4	121·9	0·95	93·8	1·48	0·57	...	...	...•	...	...
„ II .	0·9703	190·5	126·5	0·0	...	1·53	1·8	...	...	...	...	...
Thick varnish I. .	0 9720	190·0	109·4	0·24	94·68	6·36	1·45	9·17	5·12	1·65	13·53	32·31
„ II. .	0·9747	193·7	118·5	0·0	95·6	0·36	0·25	...	...	...	...	...
Burnt varnish .	0·9912	178·6	102·69	0·0	93·53	9·12	1·14	...	...	...	...	...

[1] *Analyst,* 1904, 29, 2.

E.—"BOILED" LINSEED OIL, LINSEED OIL VARNISH, VARNISH OILS.

The term "boiled" oil originates from the times when the now almost obsolete process of heating the oil over free fire to 210°-260°, with the addition of suitable metallic salts or metallic oxides (siccatives, driers) was practised. Now "boiled" oil is prepared by heating linseed oil by steam to 150°, at the same time mixing the oil intimately with added siccatives by vigorous stirring. According to the nature and quantity of the siccative and the duration of the heating, the resulting product is a "pale boiled oil" or "double boiled oil."[1]

Linseed oil is practically the only drying vegetable oil which serves for the technical preparation of good boiled oil.

The examination of the raw materials comprises the testing of :—

1. The Linseed Oil.
2. The Siccatives.

1. LINSEED OIL.

The specific gravity should not be below 0·930. The iodine value should be as high as possible, but at least 170, and the higher the better. The oil must be free from adulterants such as marine animal oils (bromide test), rosin oils, mineral oils, and rosin acids (colophony).

For the valuation of a linseed oil which has been found to be free from impurities, the time it requires to dry is of importance. In addition to the determination of the time required to dry to an elastic skin, the valuation of a linseed oil for varnish manufacture often includes the determination of the quantity of oxygen which it absorbs. Livache's method and the glass plate method (p. 127) may indeed be used for quantitative measurements, but, except in special cases, these give but little information. It is of far greater importance to ascertain the time of drying and the consistency of the elastic skin. This is done by the method generally used in practice. Much experience is, however, required in order to judge an oil by the drying test. In examining an oil it is therefore advisable to make comparative tests with a boiled oil known to be pure and of good drying quality, on glass plates covered with a thin layer of the oil (spread with the aid of a spatula, not with a brush). A good linseed oil should dry in less than three days; after this time it should not be sticky to the touch and should give a coherent, elastic skin. (Oils containing considerable quantities of unsaponifiable matter or foreign oils are recognised as adulterated by this test alone, as the presence of the impurities prevents the formation of a good elastic skin.)

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[1] For the theory of the process of "boiling" and further details, and the preparation of varnishes at ordinary temperatures, cf. Lewkowitsch, *Chemical Technology of Oils, etc.*, vol. iii., p. 138.

An important test for judging the suitability of a linseed oil for boiled oil (and especially for varnishes), consists in heating the oil in a test tube until it begins to boil. Good oil remains clear (it generally becomes somewhat paler after heating); if a mucilaginous mass ("spawn," "break") separates out, the oil must be rejected as unsuitable. In the case of oils of inferior quality the "spawn" extends through the whole mass of the oil like frog spawn. Such oils are useless for the manufacture of boiled oil and varnish in this condition. Freshly expressed ("green") linseed oil froths on heating, whereas old "tanked" oils, from which water and mucilage have settled out, do not froth. As the latter are most suitable for the above-named purposes, the preference of the manufacturers for "tanked" oil is readily understood. The mucilaginous mass consists, as G. Thompson[1] has shown, to the extent of one-half of phosphates (and sulphates) of calcium and magnesium, which on settling out carry down with them organic impurities.

2. SICCATIVES.[2]

In the older processes for the manufacture of varnishes the only drying agents used were oxides of lead and manganese, such as massicot, red lead, and pyrolusite. The salts of zinc, copper, and iron do not possess the property of imparting the desired effect to the oil. More recently, manganese acetate, oxalate, and borate have also come into use. As colophony absorbs oxygen from the air, the metallic salts of rosin acids, lead rosinate, manganese rosinate, and calcium rosinate are also employed as siccatives. The metallic salts of the rosin acids are prepared either by precipitating solutions of their sodium salts with metallic salts (e.g. sodium rosinate and manganese sulphate), or by melting together a metallic oxide with colophony. Hence, a distinction is made in commerce between "precipitated" siccatives and "molten" siccatives. By melting or precipitating colophony with a mixture of manganese and lead salts, "molten" or "precipitated" as the case may be, manganese-lead siccatives are obtained. A simple method of distinguishing between "molten" and "precipitated" siccatives is to determine the proportion of water. Only the "precipitated" siccatives contain a considerable quantity of water (up to 6 per cent.). The degree of fineness is also of importance. The further valuation of these siccatives is carried out by the ordinary methods of mineral analysis.

A further development in the industry of driers is the use of metallic salts of the fatty acids of linseed oil. These salts are prepared either by precipitating soap solutions (obtained by the saponification of linseed oil with caustic soda) with metallic salts, or by melting together

[1] J. Soc. Chem. Ind., 1903, 22, 1005.
[2] Cf. Weger, Z. angew. Chem., 1896, 9, 531 ; 1897, 10, 401, 542, 560 ; J. Soc. Chem. Ind., 1896, 15, 728 ; 1898, 17, 360.

the fatty acids and metallic oxides. In this manner "precipitated" and "molten" manganese and lead linoleates are obtained. The salts derived from linseed oil fatty acids and colophony are soluble in turpentine, ether, chloroform, and in linseed oil; hence they are termed "soluble siccatives." Solutions of such siccatives in linseed oil or turpentine, or in mixtures of these, are met with in commerce under fancy names, such as "liquid driers," "terebene," etc.

The valuation of the *Soluble Siccatives* cannot be based upon the content of metal, as found by direct ignition and weighing the ash, since suspended metallic oxides, which are not chemically combined to fatty acids or rosin acids, are not only useless, but actually detrimental to the manufacture, as they render the finished product turbid. As a preliminary test, the drier is treated with organic solvents. A good drier should dissolve completely in ether, or in the case of lead rosinate, in chloroform and in turpentine. (Turpentine also dissolves lead rosinate on warming, but the dissolved siccative separates out again on cooling.)

In the analysis of a *Soluble Drier*, the organic component is first burnt off in a porcelain crucible, and the lead, manganese, etc., determined in the ash. The weight of the ash alone does not always give reliable results, as the "molten" siccatives often contain sand, etc. Besides lead and manganese, calcium should also be determined in the ash. (Calcium rosinate is admissible as a component of driers.) A fresh portion of the sample is then extracted with ether, chloroform, or turpentine, the solution filtered, the solvent evaporated off, and the residue incinerated. In the ash the lead or manganese (or both) are determined quantitatively; the difference between the lead and manganese found, and the proportion of these metals in the original determination corresponds to the weight of lead and manganese present as insoluble excess. The result may be checked by the determination of the dissolved metal in an aliquot part of the solution. In case of a rosinate, the dissolved lead must be determined by difference, as it is stated that chloroform can be removed completely from the rosinate only at a red heat, at which temperature part of the lead chloride volatilises.

The determination and examination of the fatty and rosin acids (*cf.* p. 195) is of less importance; it can, however, be carried out by decomposing the ethereal solution with a mineral acid. It must, however, be emphasised that the chemical examination does not furnish sufficient information as to the "drying" properties of the siccative. The colour of the boiled oil to be prepared, its drying properties and other conditions, are the determining factors in the choice and quantity of a drier.

The chemical examination of the finished boiled oil comprises the detection of adulterants such as marine animal oils, vegetable oils other

than linseed oil, mineral oils, rosin oils, and colophony. Oils which have been prepared with liquid siccatives may contain small quantities of turpentine as a legitimate ingredient. The so-called "patent varnishes" are mostly adulterated oils.

Boiled Linseed Oil is distinguished from raw linseed oil by its higher specific gravity—above 0·94—also by the presence of a drier; hence on incinerating the oil a residue remains. Boiled oil is frequently mixed with raw linseed oil, as boiled oil when used alone sometimes gives a "hard" surface which readily cracks; hence a method for the detection of raw linseed oil in the boiled oil is only of some importance in those countries in which linseed oil and boiled oil pay different Customs duties.

The best method for the detection and approximate estimation of raw linseed oil in boiled oil which has been manufactured at high temperatures is the bromide test[1] (p. 138). A number of data in regard to linseed oils are given in the following Table :—

Table 30.
Values for Linseed Oils. (Lewkowitsch.)

	Sp. gr	Iodine value	Insoluble bromides from the glycerides
			Per cent.
Linseed oil (raw) . . .	0·9308	186·4	24·17
„ (light boiled) . .	0·9429	171·0	20·97
„ (double boiled . .	0·9449	169·96	13·03
„ (ozonised)	0·9310	180·1	36·26 to 36·34
„ „ . .	0·9388	171·2	25·73
„ „ . .	0·9483	169·7	30·19

The quantity of oxidised acids (p. 139) in boiled oils should not exceed a few per cent.

It should be noted that in consequence of the presence of metals in boiled oils, the iodine value found is too high, unless the metal be previously removed by treatment with mineral acids. The magnitude of the error which may result from this cause is shown by the following data :—

Varnish oil from	Original boiled oil.	After separating the metal.
Linseed oil . . {	173·3	169·7
	177·2	171·1

The valuation of a boiled oil which has been found free from

[1] Lewkowitsch, *Analyst*, 1904, **29**, 2.

adulterants must be based on practical tests, the oil being spread out in a thin layer on glass plates and exposed to the air as described on p. 127. The boiled oil is taken either in its original state, or mixed with pigments, such as are used for paints. A weighed or measured quantity of the boiled oil is very intimately mixed with a weighed quantity of pigment on a glass plate, the mixture spread out in a thin layer, and exposed to the air, side by side with a paint prepared in precisely the same way with a boiled oil of good quality. Practical experience is, however, indispensable to arrive at a correct opinion.

Boiled linseed oil is used extensively for the preparation of paints and varnishes.

F.—LINSEED OIL PAINTS AND VARNISHES.

Linseed Oil Paints.—No great difficulties are involved in the testing of linseed oil paints. The paint is shaken with ether, a mineral acid added to decompose the metal soap and to bring it into solution, in case it be soluble in acids, and the ethereal solution separated from the aqueous solution and from any insoluble residue. After evaporating off the ether the residual oil may be further tested. The mineral substances are examined by the usual methods of mineral analysis. The oil content, as a rule, amounts to 8-10 per cent. in the case of white lead, and to 30-40 per cent. in the case of black paints; other pigments require intermediate amounts.

Varnishes consist of a mixture of boiled oil, with various gum resins and oil of turpentine.[1]

The preparation of these products is guarded as a valuable trade secret. The " art" of the manufacturer lies in the choice of suitable gum resins, and in the treatment of these previous to their introduction into the boiled oil. Most gum resins must be heated beforehand to over 300°. This causes them to melt and to undergo a partial decomposition, certain oily products distilling over; the loss of weight caused by this treatment is from 5 to 25 per cent. In the manufacture the melted gum resins are dissolved whilst hot in a drying oil or a boiled oil; in the former case the oil is "boiled" after the addition of a suitable drier. The product thus obtained is termed "varnish oil." The varnish oil is allowed to stand, so that "foots" may separate out, or it is filtered through a filter press. Finally, the commercial enamel varnish is prepared by diluting the "varnish oil" with turpentine.

The most suitable oil, and in fact the only oil which is used for the manufacture of the best varnishes, is linseed oil. A large number of patents has been taken out for the manufacture of linseed oil

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[1] Lacquers are simple solutions of gum resins in alcohol, turpentine, fusel oil, etc., the examination of which lies outside the scope of this section.

substitutes, the linseed oil being replaced by tung oil, or by a mixture of linseed and tung oils. In most of the products thus prepared which have come under the author's notice, the expensive gum resins had been replaced by colophony.

The oil of turpentine is also frequently replaced by cheaper hydro-carbons, especially by petroleum hydrocarbons of the same boiling point.

A complete chemical examination of varnish oils is in our present state of knowledge a very difficult problem. Whilst the fatty oil used and the volatile solvent can be more or less easily identified, it is in some cases absolutely impossible to identify the gum resins by chemical means alone, and an extended practical experience is necessary to interpret the results furnished by the chemical tests.

In the chemical examination of a varnish the volatile solvent is first isolated by distilling 100 g. of the varnish in steam until no more volatile oil passes over. The examination of the volatile oil is comparatively simple; the specific gravity, boiling point, and iodine value of the sample yield the requisite data. The iodine values of genuine American turpentine from the live tree lie between 370 and 400. Oil from the dead wood, such as "Kienöl," has a lower iodine value.[1]

The residue remaining in the flask is freed from water and the quantity of fatty oil is estimated approximately by determining the quantity of glycerol obtained after saponification. The separation of the gum resins from the boiled oil cannot always be satisfactorily effected. The usual characteristics of the gum resins do not always yield sufficient information, as their composition is completely altered on heating to 300°. The values given in the following Table[2] may furnish useful information.

The examination of the ash shows what metal or metals were present in the siccative. Considerable quantities of lime in the ash indicate the presence of calcium rosinate, which is frequently added in much too large proportion in order to impart a fictitious hardness and lustre to the dried varnish.

The chemical examination must be supplemented by "practical" tests. The practical examination of the fatty oil as to its usefulness and drying properties is carried out in a similar manner to that described above under boiled oil. The influence of atmospheric conditions (moisture, light, etc.) can only be determined by practical tests either of the varnish alone, or in admixture with pigments.

Enamels.[3]—This is the technical term for mixtures of varnish with pigments such as zinc oxide, lead oxide, iron oxide, etc. Their chemical

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[1] *Cf.* Lewkowitsch, *Chemical Technology, etc.,* vol. iii., p. 121.

[2] *Cf.* Lewkowitsch, *Analyst,* 1901, **26,** 37.

[3] Not to be confused with the enamels of the ceramic industry.

Table 31.

Some Characteristics and Variables of Gum Resins. (Lewkowitsch.)

	Original resins.						After heating to 300°.				
	Acid value.	Saponification value.	Unsaponifiable matter.	Iodine value. By ICl.	Iodine value. By Br.	Solubility in alcohol.	Acid value.	Saponification value.	Unsaponifiable matter.	Iodine value. By ICl.	Iodine value. By Br.
			Per cent.			Per cent.			Per cent.		
Commercial copal	109·8	143·1	7·96	135·5	183·6	93·06	26·49	85·4	14·73	124·3	181·3
,,	42·43	66·82	14·99	191·2	114·6	54·83	24·94	61·04	46·40	143·7	233·5
Copal (Sierra Leone)	72·83	119·03	18·81	105·7	96·05	...	12·89	114·9	17·22	125·5	173·6
,, (Manilla)	127·6	175·17	15·98	137·9	188·2	...	68·21	136·3	22·99	133·3	186·4
,, (Brazilian)	108·99	171·4	7·66	127·7	72·66	...	46·25	113·8	38·74	136·7	225·9
,, (Sierra Leone)	65·7	110·5	16·27	94·55	117·0	...	15·82	123·8	22·31	95·23	135·4
Kauri	37·39	53·84	20·07	90·99	...	...	17·14	61·07	10·39	67·70	74·71
Mastic	52·73	81·79	51·13	175·7	185·0	84·41	23·23	50·24	49·28	165·0	217·8
Shellac (dark)	61·13	203·0	3·56	35·57	13·25	...	...	...	...	...	...
Sandarac (Mogador)	134·39	143·42	13·2	112·2	99·98	...	64·84	136·14	14·28	126·4	69·13
,, (Australian)	131·15	134·82	17·44	125·4	63·83	...	106·46	137·26	9·93	...	...
Animi (No. 1)	18·69	78·15	6·3	105·3	182·7	...	9·25	58·73	...	106·1	207·4
,, (No. 2)	30·22	93·5	6·85	96·21	95·85	...	...	...	...	...	...
Dammar	35·22	32·73	75·96	127·5	169·4	...	10·85	60·44	86·57	127·0	196·8
Amber	16·7	121·27	18·86	58·98	82·82	...	...	...	...	...	...
"Succinite"	11·24	113·68	7·06	55·05	78·4	...	10·60	99·19	16·25	74·34	147·8
Colophony	...	...	...	...	...	...	146·46	153·01	15·94	133·7	302·1

examination consists in a combination of the methods given for linseed oil paints and varnishes.

G.—OXIDISED OILS.

Under this term the author includes all those oils which have taken up oxygen on exposure to the air, or have been oxidised artifically by heating ("blowing") in a current of air or oxygen.

It is convenient to subdivide the oxidised oils into two groups.

1. Oxidised Oils, obtained from Semi-drying Vegetable Oils, Marine Animal Oils, and Liquid Waxes.

These oils (commercially known as "blown oils," "thickened oils," "soluble castor oil") are obtained by treating vegetable semi-drying oils, marine animal oils, or liquid waxes, with a current of air at a somewhat high temperature whereby the density and viscosity of the oils are increased. They thus approximate in their properties to castor oil, but differ from the latter by being miscible with mineral oils—hence their designation as "soluble castor oil." They further differ from castor oil in their insolubility in alcohol. The most striking chemical change which accompanies the "blowing" is that a considerable quantity of soluble fatty acids and of oxidised fatty acids are formed. For this reason these oils have high saponification values and somewhat high Reichert-Meissl values. Their acetyl values are also high.[1]

The blown oils are used commercially as lubricants, for the most part in admixture with mineral oils, fatty oils, and rosin oils.

2. Oxidised Oils obtained from Drying Oils.

When drying vegetable oils are exposed to the air or to a current of air or oxygen at somewhat high temperatures, the production of the oxidised acids proceeds much more rapidly than is the case with semi-drying oils. Extended use is made of this property in the employment of paints and varnishes, the vegetable oil—especially linseed oil—drying finally to a solid mass which forms a continuous skin on the surface of the object with which the paint or varnish is coated.

The chemical change which occurs when a vegetable oil dries to a solid elastic skin has been only incompletely investigated. The process seems to be the same whether raw linseed oil absorbs oxygen from the air, or whether the drying is accelerated by conversion of the oil into a "boiled" oil, or finally, whether the raw linseed oil is treated with a current of oxygen at higher temperatures after the addition of driers.

It is probable that in the first stage the linolenic acids of the linseed

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[1] Detailed Tables, showing the characteristics of "blown" oils, are given in Lewkowitsch's *Chemical Technology, etc.*, vol. iii., pp. 132 *et seq.*

oil are attacked ; the iodine values decrease and the amount of oxidised fatty acids increases.   When the oxidation of the linseed oil is carried further, *i.e.* until the linseed oil has taken up the maximum quantity of oxygen, a gelatinous solid mass is obtained, which is known as "solid linseed oil," or "oxidised linseed oil" ("linoxyn").[1]

Solid linseed oil is used very extensively for the manufacture of *Linoleum*, the solid oil being mixed with various gum resins, powdered cork, and materials added to increase the weight.   The mass thus obtained is called *Linoleum Cement*.   It is pressed on a jute cloth by means of rollers, and finally allowed to "ripen" at a temperature of about 20°.   The valuation of linoleum depends almost entirely upon practical tests.   The chemical examination consists in the determination of the ash and the treatment of the powdered mass with ether.   Any considerable quantity of linseed oil in the extract in addition to gum resins would indicate that the oil has not been treated sufficiently long with oxygen.   The methods of testing used by the *Technische Versuchs-Anstalten* in Germany [2] have been adversely criticised by H. Ingle,[3] who has proposed alternative methods.

H.—VULCANISED OILS, INDIARUBBER SUBSTITUTES.

See the section on "Indiarubber and Rubber Goods," this Vol., pp. 398 *et seq.*

J.—SULPHONATED OILS, TURKEY RED OILS.

Turkey red oils are thick, oily, dark yellow liquids, which are used in printing and dyeing cotton.   The part which they play in fixing the dye is not yet fully elucidated.   Genuine Turkey red oil is prepared by the action of concentrated sulphuric acid on castor oil.   The resulting oil is isolated by drawing off the acid layer, washing with sodium sulphate solution, and partially neutralising the acid with caustic soda solution or ammonia until the product gives a perfectly clear solution with a little water.

The portion of the product of the action of sulphuric acid on castor oil which is soluble in water contains for the most part ricinoleo-sulphuric acid, which is partially hydrolysed by boiling with dilute acids into sulphuric acid and ricinoleic acid (a further portion is converted to inner anhydrides of ricinoleic acid).   The portion insoluble

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[1] For recent views as to the process of drying, *cf.* Lewkowitsch, *Chemical Technology, etc.,* vol. iii., p. 139.

[2] H. Burchartz, *Mitt. königl. tech. Versuchsanst.,* 1899, **17**, 285 ; *J. Soc. Chem. Ind.,* 1900, **19**, 255.

[3] *J. Soc. Chem. Ind.,* 1904, **23**, 1197 ; *cf.* Lewkowitsch, *Chemical Technology, etc.,* vol. ii., p. 146.

in water contains ricinoleic acid and anhydrides of this acid, together with unchanged oil (neutral fat).   The testing of Turkey red oil consists of preliminary tests (chiefly a dyeing test) and the determination of the chemical characteristics.

Preliminary Tests.—Turkey red oil should give a perfect emulsion with 10 vols. of water; no drops of oil should separate until the emulsion has stood for a long time.   The emulsion is compared with an emulsion prepared in exactly the same way from an oil known to be of good quality.   If an excess of alkali is present it must be reduced to a minimum by the addition, drop by drop, of dilute acetic acid. The emulsion should react faintly acid towards litmus.   A good oil should dissolve to a fairly clear solution in all proportions of ammonia, and on diluting considerably only a slight turbidity should result.

For the dyeing test the oil under examination is diluted (together with a check sample) in 15-20 parts of water, and pieces of cotton cloth of equal size are soaked in exactly the same manner with the two diluted Turkey red oils.   The cloths are then dried, mordanted with alumina, and dyed with alizarin.   Recently paranitraniline red has been preferred by practical dyers.   It is difficult for anyone who has not had practical experience to judge a Turkey red oil correctly on the strength of the dyeing test alone.

Determination of the Characteristics.—The value of a Turkey red oil is primarily dependent upon the proportion of total fat contained, that is, upon the sum of the insoluble fatty acids and the neutral fat which separate out when the oil is decomposed by boiling with dilute acids.

The total fat is determined as follows:—A small deep porcelain dish of 100-150 c.c. capacity is tared together with a glass rod; then 3-4 g. of Turkey red oil are weighed into it and stirred with 20 c.c. of water, which is gradually added.   If the liquid becomes turbid, a drop of phenolphthalein solution is added and ammonia run in carefully until the red colour persists; this produces a clear solution.   Then 30 c.c. of dilute sulphuric acid (1 : 4) and 5-8 g. of beeswax are added, and the whole heated to gentle boiling until the oil layer has separated out completely.   The solution is allowed to cool, the solidified cake of fat is lifted out with the aid of the glass rod, treated as described under the analysis of " Soap " (p. 191), and weighed.   The weight of the beeswax is, of course, deducted from the total weight.

The following shortened method, described by Finsler, and recommended by F. Breindl,[1] is often used in works:—30 g. of the sample are accurately weighed out and rinsed into a flask of about 200 c.c. capacity with about 70 c.c. of hot water.   The neck of the flask is divided in $\frac{1}{5}$ or $\frac{1}{10}$ c.c.   To the contents of the flask 25 c.c. of sulphuric acid of sp. gr. 1·563 are added and the mixture is heated, with frequent

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[1] *Mitteil. d. k. k. Tech. gew. Museums*, 1888, p. 81 ; *J. Soc. Chem. Ind.*, 1889, 8, 573.

shaking, to boiling until the fatty matter forms a clear, transparent layer. A hot saturated solution of common salt or sodium sulphate is then carefully added to raise the layer of fatty matter completely into the neck of the flask. After standing for about half an hour the volume of the fat is read off. The number of cubic centimetres found multiplied by 3·33 corresponds to the percentage of the total fat. As, however, the specific gravity of the fatty matter is, as a rule, 0·945, a corresponding correction must be applied.

The total amount of fatty matter thus found is less than the actual sulphonated oil dissolved in the water by the amount of sulphuric acid split off on boiling with hydrochloric acid.

In addition to the total fatty matter the examination also comprises the determination of (a) Neutral Fat, (b) Sulphonated Fatty Acids, (c) Alkalis (Ammonia and Soda), (d) Sulphuric Acid.

(a) *Neutral Fat.*—30 g. of the sample are dissolved in 50 c.c. of water, treated with 20 c.c. of ammonia and 30 c.c. of glycerol, and extracted two or three times successively with 100 c.c. of ether. The combined ethereal extracts are washed with water, the ether distilled off from a small weighed flask, and the residue dried in the flask at 100° and weighed.

(b) *Sulphonated Fatty Acids.*—For their estimation 4 g. of the sample are boiled in an Erlenmeyer flask with 30 c.c. of dilute sulphuric acid (1 : 5) for forty minutes, with frequent shaking. After cooling, the liquid is transferred to a separating funnel and extracted with ether. The aqueous layer is drawn off and the ethereal layer washed with water. The washings are added to the main portion of the aqueous solution, and the sulphuric acid is estimated by precipitation with barium chloride. A deduction must be made from the amount of sulphuric acid found, to allow for any sodium or ammonium sulphate present as estimated under (d). The difference is calculated to recinoleic acid. 80 parts SO_3 correspond to 378 parts of recinoleo-sulphuric acid, $C_{18}H_{33}O_2.O.SO_3H$.

(c) *Ammonium or Sodium Hydroxide.*—From 7-10 g. of the sample are dissolved in ether and shaken out with four successive amounts of 5 c.c. of dilute sulphuric acid.

For the determination of the ammonia the acid liquid is distilled with potassium hydroxide solution in the usual way and the evolved ammonia absorbed in a known volume of standard acid.

For the determination of sodium hydroxide the acid liquid is evaporated in a platinum dish on a water-bath, the excess of sulphuric acid driven off by heating on a sand-bath, the residue mixed with ammonium sulphate, ignited, and the remaining sodium sulphate weighed.

(d) *Sulphuric Acid.*—The sulphuric acid which is present as

ammonium or sodium sulphate is determined by dissolving a weighed quantity of the sample in ether, and shaking out several times with a few cubic centimetres of concentrated salt solution which is free from sulphate. The total washings are diluted, filtered, and the filtrate precipitated with barium chloride.

If it be required to determine the nature of the oils used in the preparation of the Turkey red oil, the acetyl value of the total quantity of fat must be determined.

If the acetyl value is 125 or more, the oil is derived from pure castor oil; if other material has been used, the acetyl value is lower.

K.—THE CANDLE INDUSTRY.

The tallow candle industry is now practically extinct. At present the candles met with in commerce are—1. Stearine Candles, generally containing considerable amounts of paraffin wax ; 2. Paraffin Candles, always containing small additions of stearine ; 3. Spermaceti Candles ; 4. Wax Candles (beeswax candles). Ceresin is not used solely as a material for candles, but it is employed extensively in the manufacture of night-lights.

1. STEARINE CANDLES.

The materials used in the manufacture of "stearine" ("stearic acid") for candles are primarily beef and mutton tallow, bone fat, and palm oil. Less important raw materials are some solid vegetable fats, such as Chinese tallow, Malabar tallow, shea-butter, etc. In the candle industry three main products are obtained. 1. A mixture of solid fatty acids known as "stearine," the actual candle material; 2. "Oleine" or technical oleic acid, which is used in the manufacture of soaps or as wool oil; and 3. Glycerin. The resolution of the fats into free fatty acids and glycerol is effected by one of the following processes :— (1) Treatment with water under high pressure ; (2) Hydrolysis with lime or magnesia or zinc dust ; (3) Hydrolysis by means of concentrated sulphuric acid ; (4) The combination of methods 2 and 3 ; (5) Hydrolysis by means of Twitchell's reagent (prepared by allowing an excess of sulphuric acid to act on a solution of oleic acid in aromatic hydrocarbons). The solid fatty acids obtained by these processes and separated by pressing the liquid fatty acids differ considerably in value, for whereas those prepared by methods 1, 2, and 5 consist essentially of the solid acids originally present in the fats (chiefly palmitic and stearic acids), concentrated sulphuric acid converts oleic acid partially into "iso-oleic" acid, a solid mixture of several isomeric oleic acids, capable of being used as a candle material, and solid stearolactone.

(a) Testing of the Raw Material.

The proportion of water and the quantity of non-fatty substance are of importance. These are first determined. The solidifying point of the fatty acids and the colour of the fat are also of great importance. It is frequently required to determine the unsaponifiable matter, the free acids, the oleic acid, and the yield of glycerol. A description of these determinations has been given in the main in the preceding Section, to which the following details are a necessary supplement.

1. *Fats which contain large quantities of Unsaponifiable Matter*—e.g. certain kinds of shea-butter, containing 15 per cent. of unsaponifiable matter—are unsuitable for the manufacture of candles. A small quantity of unsaponifiable matter such as is found in bone fats is not detrimental.

2. *The Solidifying point of the Fatty Acids*, termed in commerce the "Titre" ("tallow titre"), is the most important criterion for the valuation of the raw materials for use in the manufacture of candles. The higher the titre the more valuable is the material. As it is necessary in determining the titre, by which tallows are mostly sold, to adhere precisely to a standard method of working in order to avoid differences of even tenths of a degree, it is necessary to give a detailed description of the method of determining the titre as adopted by the International Congress of Applied Chemistry in London in 1909.[1]

The method proposed originally by Dalican has been adopted in England, France, and the United States for the testing and valuation of commercial fats. It gives reliable results and constant figures in duplicate examinations, as the author can confirm from his own experience, so long as care is taken to perform the test under precisely the same conditions.

For the determination, 50 g. of the sample are saponified by heating with 40 c.c. of aqueous potassium hydroxide solution of sp. gr. 1·4 and 40 c.c. of strong alcohol in a flask under a reflux condenser, or in a porcelain dish on the water-bath. A flask is preferable for hard fats, to ensure complete saponification. The soap solution is freed from alcohol, dissolved in 1000 c.c. of water, and the fatty acids liberated with sulphuric acid, separated from the water, and finally filtered through a dry pleated filter into a porcelain dish. The fatty acids are then allowed to solidify in a desiccator and left to stand over night. (According to the resolutions of the Congress it is permissible to determine the titre after a few hours' standing in cases of exceptional urgency.) On the following day the fatty substance is carefully melted in an air-bath or over a free flame, and enough is poured into a test tube 16 cm. long and 3·5 cm. broad to fill the tube more than half full. The tube is then fitted by means of a cork into a wide-mouthed bottle, 10 cm. wide and

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[1] *Comptes rendus de la Commission internationale d'Analyses au VIIIme Congrès International de la Chimie appliquée,* par L. Lindet, Paris, 1909, p. 181.

13 cm. high, and an accurate thermometer divided in $\frac{1}{10}$ degrees is immersed in the fatty acids, so that the bulb is in the middle of the mass. The tube is then allowed to cool slowly. As soon as crystals are seen at the bottom of the test tube the mass is stirred by means of the thermometer, first three times from right to left, and then three times from left to right. The stirring is continued rapidly with the thermometer, care being taken that it does not touch the sides of the tube, so that all solidified particles are well stirred into the mass as soon as they appear; the fatty acids then become turbid throughout the whole mass. The temperature is now carefully watched. It first falls, and then suddenly rises a few tenths of a degree, reaching a maximum and remaining at this point for a short time before it falls again. The maximum temperature observed is called the "Titre" or solidifying point.

R. Finkener[1] uses large quantities of fatty acids in a small pear-shaped flask of about 50 mm. diameter. To avoid rapid cooling, he places the vessel containing the molten fatty acids in a wooden box (Fig. 44). This apparatus has been adopted as the official apparatus in the German Custom offices. In Austria the process proposed by F. Wolfbauer[2] is used in technical work. In this method the fatty acids (from 120 g. of the sample) are dried for two hours at 100°; the rest of the determination is carried out exactly as described above.
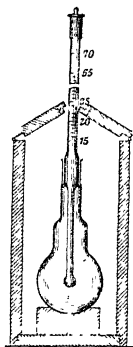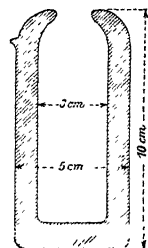
A. Shukoff[3] has constructed an apparatus by means of which it is possible

Fig. 44. Fig. 45.

to avoid small personal errors, which consists of a vessel surrounded by a Dewar vacuum jacket; this prevents too rapid cooling of the fatty acids on the walls of the vessel. The dimensions of the apparatus are given in Fig. 45.

For the determination, 30-40 g. of the melted fatty acids are poured into the inner vessel, which is then closed by a cork, through which passes a thermometer divided into $\frac{1}{3}$ degrees. When the temperature has fallen to about 5° above the presumable solidifying point, the vessel is vigorously and regularly shaken up and down, until the contents are distinctly turbid and opaque. The thermometer is then closely watched to observe the maximum temperature of solidification.

[1] *Mitt. K. techn. Versuchsanst*, 1889, p. 27 ; 1890, p. 153 ; *J. Soc. Chem. Ind.*, 1889, **8**, 423 ; 1890, **9**, 1671. *Cf.* also Lewkowitsch, *Chemical Technology*, etc., vol. i., p. 501.

[2] *Mitt. techn. Gew. Museums*, 1894, p. 57 ; *J. Soc. Chem. Ind.*, 1894, **13**, 181, 908.

[3] *Chem. Rev. Fett-Ind.*, 1899, **6**, 11.

Shukoff showed subsequently[1] that the vacuum jacket is not absolutely necessary, and that equally good results are obtained when a test tube $2\frac{1}{2}$-3 cm. wide, fitted with a thermometer, is fixed by means of a cork into the neck of a wide-mouthed bottle.

Titre tests of the fatty acids are given in Table 26, pp. 150 *et seq.* of the previous Section.

3. *The Colour* is an important criterion in the valuation of tallow. Imported tallows, which are chiefly dealt with on the English market, are therefore sold under such names as " good colour," " off colour," " no colour," etc.

4. *The Content of Free Fatty Acids* in the case of fresh animal fats is fairly small. Foreign tallows frequently contain 20 per cent. or more of free fatty acids. In palm oil the free fatty acids often much exceed this figure. The amount of free fatty acid is ascertained by determining the acid value (see p. 122).

5. *The Yield of Solid Fatty Acids* obtainable from tallow by lime saponification may be ascertained with the help of an empirical Table compiled by Dalican.[2] For technical purposes a separate Table for each class of fats should be prepared by making mixtures of solid and liquid fatty acids similar to those obtained technically on a large scale, and determining the titre of the several mixtures of known composition. Dalican's Table is obviously inapplicable to candle material obtained by sulphuric acid saponification, and separate Tables must be prepared for this purpose.[3] More accurate results are obtained in the case of saponification by water and lime (or magnesia) by determining the iodine value and calculating it to oleic acid. This method is, however, unreliable when applied to candle material obtained by sulphuric acid hydrolysis or by the mixed process, as "iso-oleic" acid also absorbs iodine.

6. *The Yield of Glycerol* is determined directly as described in the Section on " Oils, Fats, and Waxes " (p. 123). This determination is, however, generally superfluous, as it is sufficient to reckon on a yield of 10 per cent. from neutral fat, and to deduct 1 per cent. for every 10 per cent. of fatty acids.[4]

(b) Testing of Intermediate and Finished Products.

The progress of hydrolysis is watched by determining the unchanged neutral fat from time to time. An average sample is taken, and in the case of the sulphuric acid saponification process, boiled with water, and in the case of the lime or magnesia saponification process with dilute sulphuric or hydrochloric acid, then allowed to cool, and the cake of

[1] *Chem. Zeit.*, 1901, **25**, 99.
[2] *Cf.* Lewkowitsch, *Chemical Technology, etc.*, vol. ii., p. 641.   [3] *Ibid.*, vol. iii., p. 184.
[4] Lewkowitsch, *The Laboratory Companion to Fats and Oils Industries*, Table 5, p. 13.

fat taken off and washed free from acid. The acid and saponification values are then determined.

Example.—If the saponification value, k, of a sample of tallow taken from the autoclave water process be 203, and the acid value, a, be 162·2, then $k - a = 203 - 162·2 = 40·8$ corresponds to the amount of neutral fat present in the sample. As the saponification value of a neutral tallow is in round numbers 195, the proportion is :—

$$195 : 100 = 40·8 : x. \qquad x = 20·92.$$

The percentage of neutral fat in the sample is therefore 20·29, and the percentage of free fatty acids $100 - 20·92 = 79·08$.

The intermediate products are valued according to their solidifying points, and iodine values (with the above-mentioned limitation).

As regards the *Final Products*, those obtained by the water, lime, and magnesia saponification processes are technically known as " saponification " products, whilst those from the other processes are known as " distillation " products, since the fatty acids must always be purified by distillation. Hence in commerce, the terms saponification stearine, distillation stearine, saponification oleine, distillation oleine, saponification glycerin, and distillation glycerin are employed.

The value of *Saponification Stearine* depends upon the solidifying point. The higher this is, the more valuable the candle material. A definite iodine value shows the quantity of residual oleic acid in the press cakes. A distinct difference between the neutralisation value and the saponification value corresponds to the quantity of neutral fat which has escaped saponification, and has not been pressed out with the oleic acid. For commercial purposes it is seldom necessary to estimate the quantities of palmitic and stearic acids separately.

Distillation Stearine is also valued according to its solidifying point, which is generally lower than that of saponification stearine. The iodine value of a " distillation stearine " forms a measure of the quantity of " iso-oleic " acid present; the difference between the saponification value and the neutralisation value shows the amount of stearolactone present.

A complete examination of distillation stearine comprises, therefore, the determination of the iodine value, the neutralisation value, and the saponification value, and the direct determination of the stearic acid. The palmitic acid is then found by difference. It is thus possible to distinguish between " saponification stearine " and " distillation stearine " by means of the iodine value. The iodine value of the former product seldom exceeds a few units, whereas distillation stearines give iodine values which lie for the most part between 15 and 30.

A considerable amount of neutral fat is contained in the candle material used for the " composite candles," which consist of a mixture

of stearine and cocoa-nut stearine. If an accurate determination of the neutral fat is required, it is best to saponify 50 g. of the sample, and to estimate the quantity of glycerol obtained.

Adulterants of "stearine" are solid hydrocarbons (paraffin wax, ceresin), distilled wool fat stearine, also carnaüba wax, which is sometimes added to raise the solidifying point of the candle material.

The presence of these substances is ascertained by the determination of the unsaponifiable matter. The unsaponifiable matter is examined as described in the previous Section (p. 139). In this manner paraffin wax, ceresin, and carnaüba wax are detected. The presence of cholesterol indicates an addition of " distilled wool fat stearine."

Candles consisting almost entirely of stearine are generally used in hot countries, as candles which contain much paraffin wax in addition to stearine are liable to bend and gutter, in consequence of their low melting point.

In temperate climates, candles are generally made of mixtures of stearine and paraffin wax.

Commercial Oleic Acid—Oleine—is a by-product, and is, as stated above, placed on the market in two qualities, "saponification oleine" and "distillation oleine."

Saponification Oleine is generally dark in colour, and if it has not been freed from "stearine" by cooling, contains considerable quantities of solid fatty acids. Hence the iodine value of an oleine lies considerably below 90. All neutral fat which has escaped hydrolysis in the autoclave process is present in this "oleine"; its saponification value is therefore higher than its neutralisation value. All the unsaponifiable matter contained in the original fat is also present in the " oleine."

Distillation Oleine obtained in the sulphuric acid saponification process or by the "mixed process" is a distillation product, and accordingly represents a bright, transparent oil. It contains, as a rule, small quantities of solid fatty acids, so that the iodine value of a distillation oleine, prepared commercially from tallow, lies between 80 and 86.

Before the method of distilling the fatty acids had reached its present state of perfection distilled oleines contained considerable quantities of hydrocarbons, which resulted from the decomposition of neutral fat remaining in the still. Hence it was formerly possible to distinguish "distillation oleine" from "saponification oleine" by the presence of hydrocarbons in the former. At present, however, owing to the improvements in the process of manufacture, the distillation oleine of commerce is practically free from decomposition products.

The other by-product, *Glycerin*, is treated in detail later (p. 198).

2. PARAFFIN CANDLES (see also "Mineral Oils," p. 52).

The chemical composition of paraffin wax is not yet definitely known, and varies with its origin. American paraffin wax may be considered as consisting of a mixture of hydrocarbons of the ethane series. The paraffin wax obtained in the lignite .industry of Saxo-Thuringia contains a small percentage of olefines. Hence the iodine values of the paraffin waxes met with in commerce vary. Paraffin wax obtained from petroleum must not be taken to be identical with that obtained by destructive distillation. As a rule, the paraffin wax obtained by destructive distillation is superior to petroleum paraffin wax in its commercial application.

Scotch crude paraffin wax is known in commerce under the name of "scale." This contains varying quantities of impurities, dirt, water, and hydrocarbons of lower melting point, which consist principally of "soft paraffin." The latter is commercially known in England as "oil," as it is valueless to the candle-maker.

There is no definite dividing line between the solid hydrocarbons and the "oil," as the hard paraffin hydrocarbons pass by gradations through soft paraffin or lower melting paraffins to "oil." The quantity of oil which is pressed out in the manufacture depends naturally upon a number of conditions, such as temperature, pressure, length of time during which the pressure is applied to the mass, etc. It is therefore easily understood that a laboratory test for "oil" must be more or less empirical.

For this reason special tests are laid down between the buyer and seller in specifications.

The final product of the Scotch paraffin oil industry is sold as "Soft Paraffin" in case the melting point is below 48° (118° F.). Paraffin wax of melting point over 48°·9 (120° F.) is termed "Hard Paraffin." The candle material produced in the Saxo-Thuringian industry has, as a rule, a melting point of 53°-56°; material of lower melting point (50°-52°) or of higher melting point is but seldom placed on the market.

Apart from colour, transparency, and smell, the most important characteristic in valuing paraffin wax is the melting point. The melting point and solidifying points coincide in the case of paraffin wax. A uniform method for the determination of the solidifying point of paraffin wax has not yet been agreed upon. The following three methods are met with in commerce, and are known respectively as (1) The English test; (2) The American test; and (3) The German test (Halle specification).

1. *The English Test.*—A test tube of about 1 in. diameter is filled to a depth of 2 in. with molten paraffin wax. A small thermometer is immersed in the mass and the latter slowly stirred, so that the tube and

its contents cool gradually. The temperature at which the thermometer remains stationary for a short time is taken as the melting point. It is to be noted that the paraffin wax does not behave like a mixture of fatty acids, which exhibits a rise of temperature on solidifying. In the case of paraffin wax the mercury column remains stationary for about half a minute, but no sudden rise of the mercury takes place; subsequently the mercury falls gradually. The stationary point is especially distinct when larger quantities—about 50 g.—are taken for the determination.

2. *The American Test.*—A quantity of paraffin wax sufficient to fill a dish $3\frac{3}{4}$ in. in diameter three quarters full is melted. A thermometer with a round bulb is then immersed into the molten mass, so that only three-quarters of the bulb is in the paraffin wax. The wax is then allowed to cool gradually, and the temperature, at which the first sign of a film is seen to form from the wall of the dish across to the thermometer, is taken as the melting point.

3. *The German Test.*—A beaker about 7 cm. in height and 4 cm. in diameter filled with water is heated to about 70°, and a small lump of the sample is thrown on to the hot water, the lump being of such a size that after melting it spreads out to a disc of about 6 mm. diameter. As soon as the wax is liquid a thermometer of the special pattern prescribed by the " Verein für Mineralölindustrie " is plunged into the liquid so that the horizontal mercury bulb of the thermometer is completely immersed. At the moment when the paraffin film forms a solid skin the solidifying point is read off on the thermometer. During this operation the beaker must be carefully protected from draughts by glass plates; also, the paraffin layer must not be cooled by breath from the mouth.

It is evident that the determination of the melting point by the American and German methods must lead to very uncertain results. It is therefore recommended to adopt the English method.

Candles prepared exclusively from commercial paraffin wax are too soft and bend too easily; it is therefore necessary to add from 3-15 per cent. of " stearine " to paraffin wax, according to its melting point.

It has been already pointed out above (p. 173) that " stearine " is mixed with varying quantities of paraffin wax. The melting point of a mixture of stearine and paraffin wax cannot be calculated from the melting points of the components. It is, therefore, always necessary for the control of the manufacture to construct an empirical Table for the special materials concerned.

The following Tables of this character have been prepared by I. I. Redwood for mixtures of Scotch paraffin wax and " stearine," and by W. Scheithauer for mixtures of Saxo-Thuringian paraffin wax and " stearine."

Table 32.

Melting Points of Candle Material from "Mixed Paraffin Wax" (Scotch Pyroparaffin) and "Stearine." (I. I. Redwood.)

Paraffin wax.		"Stearine."		Mixture.
Per cent.	Melting point	Per cent.	Melting point.	Melting point.
	°F.		°F.	°F.
90	102	10	121	100·0
80	102	20	121	98·5
70	102	30	121	100·0
60	102	40	121	104·5
50	102	50	121	110·5
40	102	60	121	111·0
30	102	70	121	113·5
20	102	80	121	117·5
10	102	90	121	119·0
90	120	10	123	118·0
80	120	20	123	116·50
70	120	30	123	114·0
60	120	40	123	112·0
50	120	50	123	110·0
40	120	60	123	109·0
30	120	70	123	113·0
20	120	80	123	118·50
10	120	90	123	119·50
90	120·25	10	129·75	118·50
80	120·25	20	129·75	116·75
70	120·25	30	129·75	114·50
60	120·25	40	129·75	112·25
50	120·25	50	129·75	113·0
40	120·25	60	129·75	118·75
30	120·25	70	129·75	122·0
20	120·25	80	129·75	124·50
10	120·25	90	129·75	127·0
90	125	10	121	123 0
80	125	20	121	121·0
70	125	30	121	119·0
60	125	40	121	117·50
50	125	50	121	114·0
40	125	60	121	111·0
30	125	70	121	107·0
20	125	80	121	114·0
10	125	90	121	117·0
90	130	10	121	128·0
80	130	20	121	125·50
70	130	30	121	123·0
60	130	40	121	121·0
50	130	50	121	118·50
40	130	60	121	114·0
30	130	70	121	109·0
20	130	80	121	115·50
10	130	90	121	118·0
90	132·50	10	129·75	130·50
80	132·50	20	129·75	128·50
70	132·50	30	129·75	126·50
60	132·50	40	129·75	124·25
50	132·50	50	129·75	121·0
40	132·50	60	129·75	117·75
30	132·50	70	129·75	119·50
20	132·50	80	129·75	125·25
10	132·50	90	129·75	127·50

Table 33.

Melting Points of Candle Material from Saxo-Thuringian "Paraffin Wax" and "Stearine." (W. Scheithauer.)

Paraffin wax.		"Stearine."		Mixture.
Per cent.	Melting point.	Per cent.	Melting point.	Melting point.
	°C.		°C.	°C.
90·0		10·0		36·5
66·6	36·5	33·3	54	39·0
33·3		66·6		45·75
10·0		90·0		51·75
90·0		10·0		36·5
66·6	37·5	33·3	54	35·5
33·3		66·6		47·0
10·0		90·0		52·0
90·0		10·0		39·75
66·6	40·75	33·3	54	40·5
33·3		66·6		47·5
10·0		90·0		52·0
90·0		10·0		44·0
66·6	45·0	33·3	54	40·75
33·3		66·6		48·0
10·0		90·0		52·5
90·0		10·0		47·5
66·6	48·5	33·3	54	45·0
33·3		66·6		47·75
10·0		90·0		52·5
90·0		10·0		49·0
66·6	50·0	33·3	54	47·0
33·3		66·6		47·5
10·0		90·0		52·5
90·0		10·0		53·0
66·6	54·0	33·3	54	49·0
33·3		66·6		47·0
10·0		90·0		52·5
90·0		10·0		55·5
66·6	56·5	33·3	54	62·0
33·3		66·6		47·5
10·0		90·0		52·5

The proportion of stearic acid in paraffin candles is determined by dissolving 5-10 g. of the sample in petroleum spirit or ether, adding a few cubic centimetres of alcohol and titrating with normal alkali, using phenolphthalein as indicator. The number of cubic centimetres of

alkali used is multiplied by 0·284 and divided by the weight of substance taken.

3. SPERMACETI CANDLES.

Spermaceti candles are made of refined spermaceti. They are still used for lighting purposes, although they are, for the most part, super-seded by the cheaper stearine and paraffin candles. Until recently, spermaceti candles were always used as normal candles for photometric measurements in this country.

Spermaceti alone cannot be used for candle-making, as it is too brittle; hence beeswax, tallow, "stearine," paraffin wax, or ceresin is added. The standard spermaceti candles used for photometric work are only allowed to contain an addition of best air-bleached white beeswax of melting point 62°; no other material is admissible, and the amount of beeswax allowed is between 3 and 4·5 per cent. The spermaceti itself must melt between 45° and 46°.

The characteristics of spermaceti given in Table 27 of the Section on "Oils, Fats, and Waxes," p. 153, permit of the detection of adultera-tion with the above-named materials.

4. WAX CANDLES, BEESWAX CANDLES.

The wax candles for use in churches in Russia, which account for a very considerable proportion of the total wax consumption of the world, must always be made of pure beeswax. The Catholic Church now allows for ritual purposes, church candles containing 75 per cent., 65 per cent., and even less of beeswax.[1] Hence, excepting the candles destined for Russia, very few "beeswax" candles are met with which do not contain admixtures. The commonest additions are stearic acid, tallow and rosin, spermaceti, and, above all, ceresin and paraffin wax. Vegetable waxes such as carnaüba wax make beeswax practically worthless. Beeswax contains no glycerides; in addition to free fatty acids of high molecular weight (much cerotic and little melissic acid), it consists chiefly of myricin (myricyl palmitate), free myricyl and ceryl alcohols, and, in addition, smaller quantities of hydrocarbons, and also some unsaturated acids. Crude beeswax has, as a rule, a yellow to reddish-brown colour. It has the pleasant smell of honey, a fine-grained structure, and is sufficiently soft at the ordinary temperature to be kneaded; at lower temperatures it is brittle. It always contains imbedded grains of pollen which facilitate its microscopic detection. When purified by repeated melting over hot water and bleached by exposure to the sun or by chemical means, *white wax* is obtained. This is pure white or pale yellow, inodorous and tasteless, brittle and heavier than yellow wax, and generally shows a smooth fracture.

[1] *Cf.* Lewkowitsch, *Chemical Technology, etc.*, vol. iii., p. 337.

The most important characteristics of pure, yellow beeswax are given in Table 27, p. 153. It is, however, to be noted that these values do not hold for Indian waxes ("Ghedda wax"), which give abnormal values.[1] "Ghedda" wax appears to differ from ordinary yellow beeswax in that it contains ceryl alcohol as the only alcoholic constituent.

A preliminary indication of the purity of a wax is given by its melting point, specific gravity, and solubility in chloroform.

The iodine value, which varies from 9-11 in the case of pure yellow wax, whereas it is lower (about 4) for white wax, may afford further information in cases of doubt.

The most important characteristics in the examination of pure beeswax are the acid and saponification values. The acid value of yellow wax is from 18-22 (as a rule 19-20); the saponification value is 88-99, hence the difference between the acid value and the saponification value is 69-79. (This difference was termed by Hübl the "ether value"; the author avoids this term, as it is somewhat misleading.) As the higher and lower values frequently occur together, the quotient :—

$$\frac{\text{saponification value} - \text{acid value}}{\text{acid value}},$$

i.e. "Hübl's ratio value," varies within narrow limits, namely, between 3·6 and 3·8. For white wax the limits must be somewhat extended, namely, for the

Acid value	to 19·70-24·00
Saponification value . . .	„ 93·60-107·00
Hübl's ratio value	„ 2·96-3·97

The method of determining the saponification value is practically the same as for fats (p. 114), modified, however, by the fact that the esters of beeswax, as also its more frequently used adulterants (paraffin, ceresin), are almost insoluble in alcohol. Since these form a protective coating round the soluble portions, and thus inhibit the action of the alkali, incorrect results may be obtained unless the saponification be carried out as described below.

For the determination of the acid value, 3-5 g. of beeswax are warmed for some time with 25 c.c. of 95 per cent. alcohol, and the free acid then titrated with $N/2$ alkali, using phenolphthalein as indicator. The saponification value is determined on a separate quantity of 1·5-2 g. with 25 c.c. of an $N/2$ alcoholic solution of potassium hydroxide prepared with strongest (almost absolute) alcohol. The boiling must be continued over a wire gauze and under a reflux condenser for at least an hour, as the saponification is otherwise incomplete.

If the main problem be to ascertain the purity of a beeswax, it is

[1] Cf. Lewkowitsch, Chemical Technology, etc., vol. ii., p. 755.

sufficient to determine the acid and saponification values. If these give normal values the specific gravity is determined, and further, ceresin and paraffin wax are tested for by Weinwurm's method (see p. 186). If these hydrocarbons are absent and the specific gravity lies within the limits given above, the sample may be pure. The melting point and also the iodine value should, however, be determined as well.

The following Table gives the characteristics of pure beeswax and of the usual adulterants found in it (average values) :—

Table 34.

Characteristics of Beeswax and of the usual Adulterants found in it.

	Acid value.	Saponification value.	Ratio value.
Beeswax (yellow) . .	19 to 21	91 to 97	3·62 to 3·84
„ (white) . . .	19·7 „ 24	93·5 „ 107	2·96 „ 3·97
Carnaüba wax . . .	2	80	39
Chinese (insect) wax . .	0	80·4	...
Japan wax	20	227	10·8
Myrtle wax	3	208	68·3
Spermaceti	0	130	...
Tallow and tallow stearine .	4 to 10	195	18·5 to 48
Stearic acid (commercial) .	200	200	...
Rosin	130 to 164·6	146·8 to 194	0·126 to 0·191
Paraffin wax and ceresin *	0	0	0

* Commercial paraffin and ceresin are not always quite free from acid.

From these data the following conclusions may be drawn :—If the saponification value of a sample is below 92 and at the same time the " ratio value " equal to that of a pure wax, paraffin wax or ceresin is present.

If the "ratio value" exceeds 3·8, adulteration with tallow, Japan wax, spermaceti, or other waxes is probable. If, at the same time, the acid value is below 20, Japan wax is excluded. An abnormally low " ratio value" (high acid value) leads to the conclusion that stearic acid or rosin (colophony) is present. The values quoted in the Table show, however, that more complicated adulterations are possible by the simultaneous addition of several adulterants. Their presence cannot be recognised readily by the test just mentioned. Thus, the addition of a mixture of 37·5 per cent. of Japan wax, 6·5 per cent. of stearic acid, and 56 per cent. of ceresin, a mixture containing no beeswax whatever, furnishes perfectly " normal " values. In such cases the adulteration can be detected, not only by the appearance of the sample (fracture, taste), but also by the following tests :—

Detection of Glycerides.—If 20 g. of the sample are saponified and tested for glycerol, a positive result indicates the presence of fats (Japan wax, tallow).

Detection of Stearic Acid.—Stearic acid is more readily soluble in alcohol than the free cerotic acid occurring in beeswax. Hence if 1 g. of wax be boiled with 10 c.c. of alcohol of 80 per cent. by volume, allowed to cool, filtered, and water added to the filtrate, the liquid becomes only slightly turbid in the case of pure wax, whilst any stearic acid present separates in flocks; as little as 1 per cent. of stearic acid can be thus detected.

It is, however, to be borne in mind that if rosin is also present, this also dissolves and gives an emulsion with water.[1]

Detection of Rosin.—The presence of rosin in beeswax is easily recognised by its taste and stickiness. In contrast to pure beeswax it adheres to the teeth when chewed. To detect rosin the Liebermann-Storch reaction (p. 130) is used; its quantitative determination is carried out by Twitchell's method (p. 195).

Detection of Ceresin and Paraffin Wax. S. Weinwurm's Test.[2]—5 g. of beeswax are saponified with 25 c.c. of $N/2$ alcoholic potash, the alcohol evaporated off, 20 c.c. of concentrated glycerol added, and the solution heated further until all is dissolved. On adding 100 c.c. of boiling water, genuine beeswax gives a more or less clear, transparent to translucent solution. If a paper printed with letters of normal size is placed under the vessel the printing must be perfectly legible. If, on the other hand, the wax contain 5 per cent. or more of ceresin or paraffin wax, a turbid solution or a precipitate is obtained which makes the printing illegible. If the turbidity is but slight, about 3 per cent. of ceresin may be present. To detect this, a second test is made, 3 per cent. of ceresin being added to the wax before saponification. If a decided turbidity is now obtained, then small quantities of foreign hydrocarbons must have been originally present; if the turbidity is not more distinctly marked, the presence of hydrocarbons is not proved. In presence of 8 per cent. of ceresin or paraffin wax a precipitate is obtained.

It must, however, be borne in mind that this test is only of a preliminary character. Moreover, a turbidity does not necessarily point to the presence of paraffin wax and ceresin, for a beeswax to which 50 per cent. of carnaüba wax or insect wax has been added gives (as the author has shown) just as great a turbidity as one containing 5 per cent. of paraffin wax.

For the quantitative estimation of ceresin or (and) paraffin wax, the following method of A. and P. Buisine[3] is recommended:—2-10 g. of the sample are melted in a small porcelain crucible, the same weight of

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[1] For a method of detection proposed by Buchner and criticised by Berg, *cf.* Lewkowitsch, *Chemical Technology,* etc., vol. ii., p. 770.

[2] *Chem. Zeit.,* 1897, **21**, 519; *J. Soc. Chem. Ind.,* 1897, **16**, 939.

[3] *Monit. Scient.,* 1890, Ser. [iv.], **4**, 1134.

finely powdered potassium hydroxide added, and the whole stirred. The hard mass resulting on cooling is powdered and intimately mixed with 3 parts of potash lime for 1 part of wax. (The potash lime is prepared from 1 part of potassium hydroxide and 2 parts of lime.) The mixture is placed in a test tube or a small pear-shaped flask and heated in a mercury bath, the temperature being maintained for two hours at 250°. The bath consists of an iron vessel with an air-tight cover having three openings; in one of these the small flask is fixed, in the second a thermometer, whilst in the third a long iron tube is fitted, to condense the mercury vapour. After cooling, the melt is powdered, extracted with dry ether, the extract filtered, the ether distilled off, and the residue (if necessary after a second treatment with ether and filtering) dried and weighed. The proportion of hydrocarbons in yellow beeswax varies from 12·5-14·5 per cent. (Hett and Ahrens found up to 17·35 per cent.). An addition of 3-5 per cent. of ceresin or paraffin wax can thus be detected with certainty.

Detection of Carnaüba Wax.—An addition of carnaüba wax raises the specific gravity and the melting point. Carnaüba wax is not completely soluble in chloroform, in contradistinction to pure yellow wax. Weinwurm's test also serves as a good preliminary test. An incontrovertible proof of the presence of carnaüba wax is a difficult problem, and its quantitative determination still more so; these can only be effected by an exhaustive examination of both the free and combined fatty acids. This applies also to the detection of insect wax.

For the detection of the several ingredients of a white wax candle consisting of a mixture of bleached beeswax, spermaceti, stearic acid, paraffin (and) or ceresin, and for the detection of adulterants, *cf.* J. Lewkowitsch, *Chemical Technology*, etc., vol. ii., p. 776, and vol. iii., p. 335.

5. CERESIN.

Ceresin is the product obtained by refining ozokerite (earth wax), a natural bituminous product, found mostly in the neighbourhood of petroleum springs. The richest pockets of ozokerite are at present found in Galicia. The refined ceresin varies in colour from dark orange yellow to almost pure white. It has a specific gravity of 0·918-0·922, melts at 61°-78° (higher than paraffin wax), has a conchoidal fracture, and is not crystalline. Pure specimens are odourless. It is largely adulterated with paraffin wax and with rosin. Additions of carnaüba wax for the purpose of raising the melting point are also made sometimes.

The melting point of ceresin is much lowered by the addition of considerable quantities of paraffin wax. For technical purposes the melting point is still frequently determined by Pohl's method which is stipulated in specifications. The accuracy of this method has been

improved by employing Ubbelohde's apparatus (*cf.* "Oils, Fats, and Waxes," p. 108).

For the detection of paraffin wax in ceresin, J. Marcusson and H. Schlüter[1] have recommended a method which is said to give approximately correct results under certain conditions, but which, at present, stands in need of confirmation.

Ceresin containing rosin has a definite acid value. Unadulterated ceresins are, however, met with which contain a small proportion of acid, owing to the sulphuric acid used in the refining process (acid value up to 4), but samples adulterated with rosin show much higher acid values. Rosin is detected and estimated in the alcoholic extract as described on p. 186.

L.—SOAP.

Salts of fatty acids are termed soaps. A differentiation is made between salts of alkali metals on the one hand, and salts of the alkaline earths and heavy metals on the other. In commerce, the term "soap" refers only to the alkali salts of the non-volatile fatty acids. According as the base is soda or potash the products are distinguished as hard soaps (soda soaps) and soft soaps (potash soaps, soft soap). These soaps are also termed soluble soaps.

The salts of the alkaline earths and heavy metals are also termed metallic soaps, or water-insoluble soaps (*cf.* infra).

SODA SOAPS.

These are prepared on the large scale by two methods—(1) by the so-called cold process; (2) by the boiling process (hot process).

For the manufacture by the former process, the vegetable fats of the cocoa-nut oil group are especially suitable. For their saponification, concentrated solutions of caustic soda must be used. With the help of these fats, other fats which are in themselves not readily hydrolysed by concentrated caustic soda (such as olive oil, tallow, lard) may be saponified in the cold. The "cold-made" soaps which thus result contain, of course, all the glycerin, and any salts present as impurities in the caustic soda, and frequently also free alkali, and even unsaponified fat.

Theoretically, a soap prepared from cocoa-nut oil or palm kernel oil has the following composition :—

Fatty acid anhydrides	.	.	.	54·50 per cent.
Sodium oxide (Na_2O) .	.	.	.	8·86 ,,
Water and glycerol (by difference) .	.	.	36·64 ,,
				100·00 per cent.

" Filling " materials are frequently added to these soaps.

[1] *Chem. Zeit.*, 1907, **31**, 348 ; *J. Soc. Chem. Ind.*, 1907, **26**, 491.

The soaps prepared by the second method (boiling process) are obtained either by boiling mixtures of neutral oils and fats with caustic soda solution, or by boiling "fatty acids," which are manufactured on a large scale, with sodium carbonate and caustic soda. A third process depending upon the double decomposition of lime soap with soda ash is in use in a few small soap factories on the Continent. The soap paste obtained in the boiling process is "salted out" with common salt; the curd is again boiled to a paste, and then converted into pressed soap, which solidifies on cooling to a solid mass, so that it can be cut up into the well-known soap bars and cakes. The glycerol of the neutral fats passes into the soap lye. Such soaps cannot be prepared with a higher proportion of fatty acids than 63-64 per cent. The theoretical composition (taking the mean molecular weight of the fatty acids as 275) is as follows :—

Fatty acid anhydrides	.	.	.	61·80 per cent.
Sodium oxide (Na_2O) .	.	.	.	7·21 ,,
Water and glycerol (by difference) .		.	.	30·99 ,,
				100·00 per cent.

If it be desired to prepare soaps with a smaller percentage of water, as in the manufacture of *milled toilet soaps*, the curd must be deprived of part of its water ("water of constitution"). If, on the other hand, a higher proportion of water be desired, additions of solutions of silicate of soda, soda ash, sodium sulphate, common salt, etc., are made, either in the soap pan itself, or in special mixing machines. These "run" soaps represent the cheap household soaps; their proportion of fatty acids may be reduced by "filling" to as little as 12-16 per cent.

Further varieties of soda soaps are :—

1. *Transparent Soaps*, made either by dissolving the soap in alcohol, distilling off the alcohol, and moulding the gelatinous residue, thus yielding soaps containing a high percentage of fatty acid, or (cheap) "filled" soaps, rendered transparent by the addition of sugar solution.

2. *Soap Powders, Washing Powders, "Dry Soap,"* which are prepared by grinding soda soaps with soda, etc.

Potash Soaps (Soft Soap).

These are made by boiling neutral fats or commercial "fatty acids" with solutions of caustic potash, or a mixture of this with potassium carbonate. These soaps are not salted out, and hence the soft soaps contain, like the "cold-made" soda soaps, all the glycerol contained in the neutral fat, together with the excess of alkali, the potassium carbonate, and any "filling" material which may have been added. Normal soft soaps cannot be obtained in the soap pan with more than about 40 per cent. of fatty acids. Hence the theoretical composition of

a soft soap made from neutral fats or "fatty acids," assuming a mean molecular weight of 275 for the fatty acids, is as follows :—

Fatty acid anhydrides	.	.	38·70 per cent.
Potassium oxide (K$_2$O)	.	.	6·84 „
Water and glycerol (by difference) .	.		54·46 „
			100·00 per cent.

Potash soaps are frequently "filled," so that the proportion of fatty acid in commercial products falls to 25 per cent. and less. Frequently rosin is introduced, so that the isolated fatty acids include the rosin acids. The latter are estimated by Twitchell's method (p. 195).

The number of substances which are openly added to soaps, to impart to them some useful (real or supposed) property, is enormous. It must be left to the analyst to decide in each individual case whether petroleum, paraffin wax, tar oil, sulphur, etc., are to be regarded as adulterants or not.

In the present state of the soap industry, and in view of the requirements of the consumer, it is difficult to say what constitutes *Adulteration*.

Rosin (colophony) is a legitimate substitute for fatty acids, as the alkali salts of the rosin acids possess washing properties. Hence rosin acids, which are obtained on decomposing a soap with mineral acid, are generally reckoned together with the fatty acids and returned as fatty acids.

Silicate and *borate* also possess washing properties ; these substances must, however, be considered as standing on the border line between legitimate ingredients and adulterants.

Dyes in soaps must not be considered as illegitimate additions, as there is a demand for coloured soaps. Provided that the colouring matter is harmless, no objection need be raised against such an addition. At the most, the analyst will have to determine whether the colouring matter contains poisonous metals or not.

Essential Oils in soaps have become almost a necessity. The quantity contained is generally very small, and, as a rule, such ingredients do not come within the scope of the analytical examination.

There can, however, be no doubt as to adulteration having taken place when filling materials or "weighting substances" are found in a soap. Starch, clay, talcum, sand, etc., fall under this category. Naturally, the sand found in a "sand soap," sold as such, cannot be looked upon as an adulterant.

RAW MATERIALS.

The raw materials of the soap industry are the neutral fats and

"fatty acids," which are examined by the methods described in the foregoing Section. In the "fatty acids" the quantity of neutral fat and fatty acids is determined (*cf.* p. 177).

In the following paragraphs the most reliable methods (omitting a large number of suggestions) for the testing and valuation of commercial soaps are given. The author has made no attempt to give a general and complete system for the analysis of soaps which would include every possible ingredient, as such a procedure would have but little value.

Sampling.—In sampling great care must be taken to avoid errors in the determination of moisture. By exposure to the air soap dries on the surface, and as soon as a "skin" has formed on the outer surface of a hard soap the interior is protected against further evaporation. Therefore, in the case of hard soaps the samples for analysis must be taken from the middle of the piece, the skin being cut away; an inspection of the sample will generally indicate how much must be cut away, as a transverse section shows to what depth the drying has progressed. Suggestions to take a sample by means of a cork borer or by cutting out a transverse section, so as to obtain an "average sample," lead to incorrect results. If the sample to be tested is fresh, thus containing at least 30 per cent. of water, a somewhat large quantity is quickly weighed out (as soap readily loses water in the dry air of a balance case). For the same reason, the sample should not be sliced before weighing; at most, this is permissible only in the case of a milled or of a dried soap.

In such cases the well-known devices to prevent loss of water during weighing must be employed.

Similar precautions must be observed in sampling soft soaps. The sample must be taken from the middle of the soap.

(*a*) Determination of the Fatty Matter and Total Alkali.

A rapid method, sufficiently accurate for commercial purposes, is the following :—5-10 g. of the sample (or 50 g. weighed on a balance which indicates correctly to centigrams) are accurately weighed out, and dissolved in hot water in a beaker or a porcelain dish, the liquid being stirred constantly with a glass rod to prevent the caking of the soap at the bottom of the vessel. After adding a few drops of methyl orange an excess of standard sulphuric acid (or in case chlorides and sulphates are to be determined, dilute nitric acid) is added, and the liquid heated, with constant stirring, until the separated fatty acids have liquefied. About 5 g. (or 20 g. for 50 g. of soap) of dry beeswax or paraffin wax, weighed accurately in a tared watch-glass (which is afterwards used for weighing the fatty matter), are added, and the liquid again heated until the mixture of fatty acids and wax has separated on the surface of the

aqueous layer as a clear, transparent layer of oil, free from solid particles. (If it be known that the fatty acids solidify to a hard mass, the addition of wax, etc., is, of course, superfluous.)   The glass rod is rinsed with hot water, and the liquid again heated until the fatty substance forms a uniform mass.   The source of heat is then removed and the vessel allowed to cool.   Any white precipitate found on the bottom of the vessel indicates the presence of silicate or of "filling" materials, which are insoluble in mineral acid.

The solidified cake of fatty matter is lifted off by means of a platinum spatula, rinsed with cold water, and placed on filter paper. Any remnant of fatty matter adhering to the walls of the vessel are carefully scraped off and added to the main portion.   The cake is dried with filter paper and brought on to the same watch-glass which was used before, bottom side upwards, and allowed to dry in a desiccator and weighed.   (For the control of the manufacturing process, for which purposes 50 g. should be taken, it is sufficiently accurate to weigh at once after drying with filter paper, but care must be taken that all water present in crevices of the cake are removed by filter paper.)   If the cake has crevices enclosing water and perhaps even acid, which occurs only when the mass has not been heated sufficiently long, the cake must be melted over water, allowed to solidify, and again treated as before.

The weight of the beeswax or paraffin wax is deducted from the weight thus found, and the difference is reckoned as fatty matter; when no further examination is required, it is generally returned as fatty acids; this is, however, only correct if the absence of neutral fat, wax, and unsaponifiable matter has been proved.   Rosin acids are included in the fatty acids, except in cases where a separate determination of rosin acids is required.   The acid liquid is filtered, the excess of mineral acid titrated back with standardised alkali, and the total alkalinity thus found.

Any soluble fatty acids present in the soap pass to some extent into the acid liquid; as a rule they are neglected, except when cocoanut oil or palm kernel oil soaps are under examination.   In such cases it is best to work with concentrated solutions, or, if permissible, to add common salt, which renders the bulk of these acids insoluble, so that the dissolved portion may be neglected.   If great accuracy is required, the soap is decomposed under ether; all the fatty acids are thus obtained in ethereal solution as they are liberated.   A less accurate method is to titrate the aqueous solution to neutrality with methyl orange, then to add phenolphthalein, and to titrate again with $N/10$ alkali.   In this case the alkali used for the second titration is calculated to caprylic acid, $C_8H_{16}O_2$, molecular weight 144, and the amount thus found is added to the main portion of the fatty acids.

A considerable number of methods supposed to increase the

accuracy of the determination have been suggested. In the author's opinion, however, they only complicate the analysis without offering any advantage.

If the absence of neutral fat, wax, and unsaponifiable matter (p. 196) has been proved, the fatty material is returned as fatty acids. In a complete soap analysis this amount is multiplied by 0·9675 to convert it to anhydride.

The higher the percentage of fatty acids, the more actual soap is present. A comparison of the analytical results with the theoretical compositions of soaps given above will furnish a useful guide in the valuation of a sample.

(b) Combined Alkali, Free Caustic Alkali, and Alkaline Salts. Free Fatty Acids.

The total alkali is the sum of the several amounts of alkali present in the soap, as (1) alkali combined with fatty and rosin acids termed "combined alkali"; (2) free caustic alkali; (3) alkali as carbonate, silicate, or borate.

1. **The Combined Alkali** is generally found by difference, i.e. by subtracting the sum of the amounts of alkali found under (2) and (3) from the total alkali. It can, however, be determined directly by titrating the alcoholic solution with methyl orange, after having made it neutral to phenolphthalein. This may be done as a check, or to avoid the separate determination of alkali present as carbonate, silicate, or borate, as the latter can then, of course, be determined by difference.

2. **Free Caustic Alkali.**—A preliminary test is first made by placing a drop of phenolphthalein on to a freshly cut surface of the soap. A red colour indicates the presence of free sodium hydroxide; if the soap is moist the red colour may be produced also by carbonate, silicate, or borate, but if it has been dried these salts produce no coloration. In order to separate the free caustic alkali from alkaline salts, part of the sample is dissolved in absolute alcohol and filtered. The alkaline salts remain on the filter, so that the alcoholic filtrate can then be tested with phenolphthalein.

Soaps which have been properly manufactured should not contain free alkali; this holds especially for toilet soaps. As great care and experience are necessary in the process of "filling," in order to produce a soap practically free from excess of alkali, most commercial soaps, especially household soaps, contain an excess of free alkali. If this quantity be very small, the free alkali becomes converted to carbonate by exposure to the air, so that in some cases no free alkali is found, especially if the outer layer only is tested.

Free caustic alkali is estimated quantitatively [1] by dissolving 10-30 g.

[1] Hope, *Chem. News*, 1881, 43, 219.

of the sample in hot absolute alcohol in a loosely closed flask (to avoid the absorption of atmospheric moisture). Soaps containing much moisture must be partially freed from water, care being taken to exclude air, to avoid absorption of carbon dioxide. The hot solution is rapidly filtered, so that the soap does not separate out as a gelatinous mass on the filter; when the operation is carried out with care, a hot-water funnel is unnecessary. The filter is washed with absolute alcohol and the filtrate collected in a flask. Phenolphthalein is then added, and the solution titrated with $N/10$ hydrochloric acid.

In some cases the alcoholic soap solution may react acid to phenolphthalein. This is due to the presence of an acid salt (distearate, dipalmitate, dioleate), in consequence of faulty fitting, or also to intentional addition of fatty acids to the soap with the object of neutralising the free alkali. The quantity of $N/10$ alkali necessary to neutralise the solution is calculated to *free fatty acids* in terms of oleic acid.

3. Carbonate, Silicate, and Borate.—The residue remaining on the filter consists of carbonate, silicate, and borate, together with other insoluble substances added as filling materials, such as starch, talcum, dyes, etc. (For a complete examination of this residue, see p. 197). For the determination of the alkali contained in the alkaline salts, the residue is washed on the filter with cold water (*cf.* (*e*) I, p. 197). The alkali in the filtrate is determined by titration with normal acid, using methyl orange as the indicator, and is calculated to Na_2O.

(c) Determination of Water.

The direct determination of water in a soap is, as a rule, unnecessary. In the case of genuine soaps it is sufficient for all practical purposes to calculate the fatty acids to anhydrides and to add the quantity of alkali found in the several forms; the water is then found by difference.

The direct determination of water is therefore carried out only in exceptional cases. For this purpose the soap is introduced in thin shavings into a porcelain dish, weighed with a glass rod, so that from time to time the dry skin, which prevents the evaporation of water from the interior layers, can be broken. This is especially necessary in the case of highly "run" soaps.

For the valuation of a sample of soap it is generally sufficient to carry out tests (*a*) to (*c*). Further tests include the examination of the fatty matter and the detection and estimation of other ingredients of the sample.

(d) Examination of Fatty Matter ("Soap Stock").

Assuming no wax, etc., has been used in the separation of the fatty matter, this can be used at once for further examination. The fatty

matter may contain in addition to fatty acids: 1. Rosin acids; 2. Neutral fat; 3. Unsaponifiable matter.

1. **Rosin Acids**.—These are determined by Twitchell's method,[1] as the author has shown that the older methods proposed by Barfoed and Gladding and others, and the modifications of these methods, give unreliable results.

E. Twitchell's method depends upon the property of the aliphatic acids that they are converted into esters by treatment with hydrogen chloride gas in alcoholic solution, whereas rosin acids under the same treatment undergo only a very slight alteration, abietic acid separating from the solution.

For the determination, 2-3 g. of the mixed fatty and rosin acids are weighed out accurately in a flask and dissolved in ten times their quantity of absolute alcohol. The use of *absolute* alcohol is indispensable, as esterification is incomplete in 90 per cent. alcohol. The flask is immersed in cold water, and a current of dry hydrogen chloride is passed through the liquid. After about three-quarters of an hour, when the gas is passing through the liquid unabsorbed, the operation is finished. In order to achieve as complete esterification as possible, the flask is allowed to stand for an hour. During this time the ethyl esters and the rosin acids rise to the surface as an oily layer. The contents of the flask are diluted with 5 vols. of water, and heated until the aqueous solution has become clear. The analysis can then be completed either volumetrically or gravimetrically.

(a) *Volumetric Method.*—The contents of the flask are transferred to a separating funnel, and the flask rinsed out several times with ether. After shaking well the acid layer is drawn off, and the ethereal solution, which contains the ethyl esters of the fatty acids and the unchanged rosin acids, is washed with water until the hydrochloric acid is completely removed. Then 50 c.c. of alcohol are added to the solution, and it is titrated with normal alkali, phenolphthalein being used as the indicator. The rosin acids combine at once with the alkali, whilst the ethyl esters remain almost unchanged. The combining weight of the rosin acids is taken as 346; thus the number of cubic centimetres of normal alkali used in the titration multiplied by 0.346 gives the quantity of rosin acids in the sample.

(b) *Gravimetric Method.*—The contents of the flask are mixed with some petroleum spirit boiling below 80°, and transferred to a separating funnel, the flask being rinsed out with petroleum spirit. The petroleum layer should amount to about 50 c.c. After shaking, the acid solution is drawn off, the petroleum layer washed once with water, the water drawn off, and 50 c.c. of an aqueous solution of potassium hydroxide containing 0.5 g. of potassium hydroxide and 5 c.c. of alcohol are added.

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[1] *J. Anal. and Applied Chem.*, 1891, **5**, 379; *J. Soc. Chem. Ind.*, 1891, **10**, 804.

The rosin acids are extracted by the dilute alkaline solution, forming soaps, whilst the ethyl esters still dissolved in the petroleum spirit float on the surface. The soap solution is drawn off, decomposed with hydrochloric acid, and the separated rosin acids are weighed, either directly on the filter, or preferably after extraction with ether and evaporation of the ether. The residue gives the quantity of rosin acids present in the sample.

Of all the methods hitherto proposed for the estimation of rosin acids, Twitchell's method gives the best results. These must not, however, be considered as strictly accurate, as the author has shown in an exhaustive investigation of the volumetric and gravimetric methods that the results are only approximate.[1]

2. **Neutral Fat.**—A properly manufactured soap will seldom contain unsaponifiable fat. In case neutral fatty matter has been purposely added to the finished soap, as in the case of "superfatted" soaps (olive oil, or, in certain toilet soaps, wool wax), it is obtained together with the unsaponifiable matter. The neutral fat must then be separated from the unsaponifiable matter.

The neutral fat plus unsaponifiable matter can be obtained directly from the sample by dissolving a weighed quantity in water or alcohol, titrating with normal alkali in the presence of phenolphthalein to neutralise any free fatty acids, and then extracting the soap solution as described in the Section on "Oils, Fats, and Waxes," p. 124.

The residue of the ethereal solution consists of neutral fat plus unsaponifiable matter. The separation of the two components is effected by saponifying and extracting again with ether.

If no unsaponifiable matter be present, the ether residue consists essentially of neutral fat; otherwise the neutral fat is found by difference, or it may also be ascertained directly by isolating the fatty acids and calculating the quantity found to glycerides.

A complication occurs when the soap contains wool wax. If this ingredient is suspected, the ether residue must be saponified with dilute alcoholic potash on the water-bath, in order to obtain at least a portion of the wool wax in the form of unsaponifiable matter, which can then be examined and identified.

3. **Unsaponifiable Matter.**—This is determined together with the neutral fat, as described. In case no neutral fat be found, the whole of the ether residue is taken as unsaponifiable matter. This is examined as described in the Section on "Oils, Fats, and Waxes," p. 139.

Besides the substances given on p. 139, the possibility of the presence of vaselin, petroleum hydrocarbons, naphthalene, paraffin wax, wool-fat hydrocarbons, etc., must be taken into account.

The examination of the fatty acids themselves (after separating the

[1] *J. Soc. Chem. Ind.*, 1893, **12**, 504.

rosin acids, neutral fat, and unsaponifiable matter) is also carried out as described in the Section on " Oils, Fats, and Waxes."

(e) Substances Insoluble in Alcohol.

The determination of all the substances which are insoluble in alcohol is conveniently combined with the estimation of free caustic alkali (p. 193), the insoluble residue being collected on a previously dried (at 100°) and weighed filter, and then weighed after again drying at 100°.

Good soaps generally give a negligible residue. Only the toilet soaps prepared by the "alcohol process" are quite free from insoluble substances.

The residue on the filter may consist of :—

1. Water-soluble substances, such as chloride, sulphate, carbonate, silicate, and borate of the alkali metals.

2. Mineral substances insoluble in water, such as colouring matters, " filling " and " weighting" materials such as talcum, etc.

3. Organic substances, especially starch, dextrin, gelatin (Carragheen mucilage).

1. **Water-soluble Substances**.—The residue on the filter is washed with *cold* water, so that any gelatin present does not pass into solution. The presence of silicate will have been already detected in the determination of the fatty matter when decomposing the soap by acid (see above under (*a*)). The silica can be determined at this stage, assuming that no other substances insoluble in water are present, by acidifying the filtrate with hydrochloric acid, after determining the total alkali by titration (see (*b*) 3) and evaporating to dryness in the usual way. The filtrate from the precipitated silica can be examined for boric acid.

In case boric acid is absent, carbonate and silicate may be found from the total alkali as estimated by titration, and the silica as found by weighing. If boric acid is also present and its quantity is to be determined, it is best to divide the solution into three parts. In the first the carbonic acid is determined, in the second the silica, and in the third the total alkali by titration.

Chlorides and sulphates are best determined in aliquot parts of the acid liquid obtained after separating the fatty matter as described under (*a*). In this case, as stated above, nitric acid must be used for the decomposition of the soap.

2. **Substances Insoluble in Water** are incinerated to remove organic matter, and the residue weighed. The ash is examined qualitatively and quantitatively in the usual way.

3. **Organic Matter**.—The microscopic examination of the total residue insoluble in alcohol may furnish valuable information.

Starch can be detected in this manner ; the microscopic examina-

tion may be confirmed by the iodine test.   If a quantitative examination is required, the starch is converted to glucose.   The residue insoluble in alcohol is washed on the filter with cold water to remove substances soluble in water, and dextrin, and is then boiled with dilute sulphuric acid, the water being replaced as it evaporates.   The liquid is neutralised with potassium carbonate, filtered, and the glucose determined by Fehling's solution.

Dextrin is removed by cold water together with the soluble salts. It is determined by precipitation with alcohol.   This is best done in a small beaker weighed together with a glass rod.   The liquid is vigorously stirred so that all the dextrin settles out on the sides of the beaker.   The aqueous solution is then decanted, the residue washed with alcohol, and determined by weighing after drying at 100°.

Gelatin is removed by washing the residue insoluble in alcohol with hot water.   The filtrate is then tested with tannic acid to corroborate the presence of gelatin.

(*f*) Other Substances which occur in Soaps.

1. Glycerol.—The small quantities of glycerol left behind in hard soaps prepared by the boiling process can be determined with accuracy only by working with a large quantity of soap.   On decomposing the soap with mineral acid, the glycerol passes into the aqueous solution; this is examined by the method described below (p. 202) for the "determination of glycerol in soap lyes."   From the quantity of glycerol found a conclusion may be drawn as to whether a hard soap has been prepared by the cold process or not.   In this case about 5 per cent. of glycerol will be found.   The absence of glycerol in a soft soap proves that the soap has been manufactured from "fatty acids."

Considerable quantities of glycerol are added to certain toilet soaps in the milling process.   Glycerol must, in virtue of its cosmetic properties, be considered a valuable constituent of such soap.   It is determined by dissolving the soap in water, separating the fatty matter by means of a mineral acid, and filtering.   The filtrate is neutralised with barium carbonate, evaporated to a syrup, and the residue extracted with a mixture of 3 parts of 95 per cent. alcohol and 1 part of ether.   The alcoholic solution is filtered, evaporated on the water-bath to a small volume, and finally dried in a desiccator.   The glycerol in the crude glycerin thus obtained is then estimated by the acetin method (p. 123).

In case a soap also contains sugar, the sugar must first be removed.

2. Sugar (Saccharose) is found in considerable quantities (up to 25 per cent. and more) in cheap, transparent soaps.   The determination of the cane sugar is best effected by boiling the filtrate obtained in (*a*), or an aliquot portion, with dilute sulphuric acid, to invert the sugar, then making the solution alkaline, and heating with Fehling's solution,

after diluting considerably to prevent oxidation of the glycerol. The cuprous oxide which separates out is determined in the usual way and calculated to cane sugar. If the quantity of sugar is considerable, it may·be determined polarimetrically.

If glycerol and sugar are present simultaneously, they are separated by the method of E. Donath and J. Mayrhofer,[1] which consists in adding a sufficient quantity of slaked lime to combine with the sugar, then an equal quantity of washed and ignited sand, evaporating to a syrup, powdering the residue after cooling, and extracting in a closed flask with 80-100 c.c. of a mixture of equal volumes of alcohol and ether. The solution will then contain the glycerol free from sugar, and the glycerol present is determined as in (1).

3. Carbolic Acid.—The determination of "carbolic acid" (phenol and cresols) in carbolic soaps is carried out with sufficient accuracy by the following method (Lewkowitsch) :—

A considerable quantity of the sample (about 100 g.) is weighed out, dissolved in hot water, and sufficient sodium hydroxide solution added to make it strongly alkaline. The soap is then salted out with common salt, the curdy soap filtered off, and the soap washed with salt solution. The solution, which now contains the phenol and cresols as sodium salts, is evaporated down, and any dissolved soap is precipitated by a further addition of common salt. The solution is filtered again, evaporated down to a small volume, introduced into a graduated stoppered cylinder of 50-100 c.c. capacity, and common salt added until some remains undissolved ; the solution is then acidified with sulphuric acid. The volume of the separated phenols is read off, and the number of cubic centimetres is reckoned as equivalent to the same number of grams.

If greater accuracy be required, the separated phenols are extracted with ether, the ether evaporated off, and the phenol and cresols determined by the methods described in the Section on "Coal Tar," Vol. ii., part ii., pp. 811 et seq.

Metallic Soaps.

These are either salts of the fatty acids or of rosin acids, or mixtures of both, as, for instance, the driers described on p. 163. To this class of soaps belong the *Lead Plasters*, chiefly lead oleate ; *Aluminium Oleate*, which is used to thicken lubricating oil ; *Lime Soaps*, which are used in the manufacture of lubricating greases ; *Magnesium Oleate*, used in petroleum spirit solution by dry-cleaners as a protection against the generation of electric sparks ; and, finally, *Zinc, Iron, Chromium*, and *Copper Soaps*, used in anti-fouling and anti-rusting paints.

For analysis, the metallic soaps are decomposed by a suitable

[1] *Z. anal. Chem.*, 1881, **20**, 383.

mineral acid (hydrochloric, nitric, sulphuric), the fatty and rosin acids being obtained as an oily layer, or, if the salts are decomposed under ether (which is frequently the more suitable method), the acids pass into the ether layer and the metal into the acid solution. The separated fatty and rosin acids are examined as described above.

M.—GLYCERIN.

The glycerins met with in commerce are classified as: 1. Crude glycerin; 2. Distilled glycerin; Dynamite glycerin; 3. Chemically pure glycerin.

1. CRUDE GLYCERIN.

Three kinds of crude glycerin are distinguished in commerce: (*a*) Crude saponification glycerin; (*b*) Crude distillation glycerin; (*c*) Soap-lye crude glycerin; Soap crude glycerin.

(*a*) Crude Saponification Glycerin.

This is a product of the autoclave process (see p. 173). It is evaporated down to a sp. gr. of 1·240-1·242, and sold as "28° Bé. saponification glycerin" or "crude candle glycerin." It has a pure sweet taste, and varies in colour from bright yellow to dark brown. It gives only a slight precipitate with lead acetate, and scarcely any turbidity with hydrochloric acid. The valuation of this glycerin comprises the determination of the ash, which should not exceed 0·3-0·5 per cent., the determination of the glycerol, and of the organic impurities.

The glycerol is best determined by the acetin method as described in the Section on "Oils, Fats, and Waxes" (p. 123). Of the oxidation methods, only Hehner's modification of the bichromate method can be recommended. The author has, however, shown that this method gives too high a percentage, especially in the case of impure glycerins.[1] Since, nevertheless, the bichromate method is still frequently used in commercial analysis, it may be described here. The following normal solutions are required: (1) A solution of potassium bichromate containing 74·86 g. $K_2Cr_2O_7$ per litre. Hehner recommends the addition of 150 c.c. of concentrated sulphuric acid before the solution is made up to 1000 c.c. The author considers it preferable to keep the unacidified solution as a stock solution, and to add the sulphuric acid only at the time of the experiment. The actual oxidising value of the solution must be determined by titrating a known solution of ferrous sulphate or pure ferrous ammonium sulphate, or pure iron wire. (2) Solution of ferrous ammonium sulphate, containing about 240 g. per litre. (3) A bichromate solution, prepared by diluting 100 c.c. of

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[1] *Analyst*, 1903, **28**, 104.

solution (1) to 1000 c.c. The solution (2) must correspond accurately to the strong bichromate solution of which 1 c.c. is equivalent to 0·01 g. of glycerol.

For the determination about 1·5 g. of crude glycerin is accurately weighed out into a 100 c.c flask, diluted with water, silver oxide added (or copper sulphate and potassium hydroxide solution), and after standing for a short time a few drops of lead acetate are added and the whole made up to 100 c.c. After filtering, 25 c.c. of the solution are transferred to a beaker, previously cleansed with concentrated sulphuric acid and potassium bichromate, and 40 c.c. of the concentrated bichromate solution are added. As the bichromate solution is unavoidably a concentrated one, it is necessary not only to measure it with great care, but also to observe the temperature of the solution. Hehner states that this bichromate solution expands 0·05 per cent. per degree. The author avoids corrections by keeping the solutions at normal temperature in a large water-bath until the titration is finished.

Then 25 c.c. of concentrated sulphuric acid are added, the beaker is covered with a watch-glass, and placed for two hours in boiling water. The excess of bichromate is then reduced with an excess of ferrous ammonium sulphate solution, and the excess of the latter finally titrated back with the dilute bichromate solution, potassium ferricyanide being used as indicator.

The glycerol content of commercial samples varies, as a rule, between 85 and 90 per cent.

Organic Impurities are determined quantitatively by heating a few grams gradually to 160° in a platinum dish in a drying oven. Rapid heating tends to cause the formation of polyglycerols, which of course lead to incorrect results. It is best to moisten the glycerin from time to time with a few drops of water, so that the glycerol may evaporate with the water. The residue is dried to constant weight. The amount thus found is the sum of the ash and organic impurities. The ash is found by incineration, and subtracted from the total residue found.

Crude glycerin obtained by the fermentation process is also sometimes termed "saponification glycerin"; it should be noted that it contains, as a rule, a considerably larger amount of ash and organic impurities.[1]

(b) Crude Distillation Glycerin.

This crude glycerin is obtained from the acid water resulting from the acid saponification process. The solutions are evaporated down to a sp. gr. of 1·240-1·242. The crude glycerin has generally a bright yellow colour and a sharp astringent taste; when rubbed on the hand it has an unpleasant odour. As a rule it contains 84-86 per cent. of

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[1] *Cf.* Lewkowitsch, *Chemical Technology, etc.*, vol. iii., p. 332.

glycerol. The ash generally varies from 2-3.5 per cent. The percentage of glycerol can be determined with greater accuracy by the acetin method than by oxidation. This crude glycerin gives a decided precipitate with lead acetate; on addition of hydrochloric acid a marked turbidity is generally obtained (fatty acids).

A product of a similar character is the glycerin obtained by Twitchell's process (p. 173).

(c) Crude Soap-lye Glycerin; Crude Soap Glycerin.

This glycerin is obtained from waste soap-lyes. The specific gravity of the commercial product should not be below 1.3, the content of glycerol should be at least 80 per cent., and the proportion of salts should not exceed 10.5 per cent.

The percentage of glycerol is best determined by the acetin method in preference to the bichromate method (p. 200).

For the determination of the ash, 3-5 g. are slowly incinerated in a platinum dish over a small burner. When the bulk of the glycerol has been driven off, the dish is more strongly heated; a voluminous carbonaceous residue remains in the dish. The organic matter is then burnt off, care being taken that no sodium chloride volatilises. The residue, which contains some carbon, is exhausted with water, and the filtrate evaporated in the platinum dish on a water-bath. This residue must be white; it is heated to dryness (not over 400° to avoid volatilisation of sodium chloride), and weighed. The carbon residue is burnt, and the residual ash is also weighed; this is especially necessary when the sample contains lime.

Crude glycerin which contains sulphates and thiosulphates is almost worthless to the refiner; the qualitative detection of these substances is therefore of importance.

Recently an International Committee, consisting of manufacturers and some analytical chemists, has published, under the title of "International Standards for the Analysis of Crude Glycerin," somewhat more detailed methods of examining crude soap-lye glycerins.[1]

2. DISTILLATION GLYCERIN; DYNAMITE GLYCERIN. (*Cf.* the Section on "Explosives," Vol. ii., part i., p. 490.)

These glycerins are obtained from the above-described crude glycerins by distillation.

The distilled glycerins vary in colour from yellow to almost white. Their proportion of glycerol varies according to the specific gravity, which generally lies between 1.220 and 1.260; it can be found approximately from the specific gravity (*cf.* Table 35, p. 205). As, however,

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[1] *J. Soc. Chem. Ind.*, 1911, 30, 556; 1912, 31, 1084; 1913, 32, 1039.

these glycerins contain a little ash, it is necessary in accurate analyses to determine the glycerol by the acetin method (or by an oxidation method, such as the bichromate or even the permanganate method, p. 207). In this case also the oxidation methods easily lead to high results. Dynamite glycerin is a special quality of distilled glycerin which has a specific gravity of from 1·261-1·263. The colour varies from deep yellow to bright pale yellow. From a large number of specifications regulating the conditions of sale of this glycerin, the author has extracted the following requirements :—

(a) *Specific Gravity.*—This must not be less than 1·261 at 15·5°.

(b) *Lime, Magnesium,* and *Alumina* must be absent.

(c) *Chlorides* may only be present in traces. 1 c.c. of glycerin diluted with 2 c.c. of water must not give a decided milky turbidity with silver nitrate.

(d) *Arsenic.*—Only traces are permitted. As the Gutzeit test (p. 208) is too sensitive, the following method is used. The sample is made just alkaline with a very small quantity of ammonia, and silver nitrate is added when no milky turbidity should be observable. An excess of ammonia is to be avoided, as silver arsenite is soluble in ammonia.

(e) *Foreign Organic Matter.*—1 c.c. of the sample is diluted with 2 c.c. of water, and a few drops of a 10 per cent. solution of silver nitrate are added. On standing for ten minutes there should be no brown or black coloration.

(f) *Total Residue.*—This is determined as described above (p. 201). (Polyglycerols).

(g) *Free Acid.*—The glycerin must not redden blue litmus paper. Volatile fatty acids are detected most readily by the pleasant odour emitted (recalling that of pine apple) on warming the sample with alcohol and concentrated sulphuric acid. On diluting 1 c.c. of the sample with 2 c.c. of water, and adding concentrated hydrochloric acid, no turbidity should be noticeable.

(h) *Nitration and Separation Test.*[1]—A commercial sample may pass all the above-mentioned tests satisfactorily and yet be unsuitable for the manufacture of nitroglycerin. Its suitability for this purpose must, therefore, be especially ascertained by the following method, which is based upon the large scale process. A mixture of 1 part by weight of fuming nitric acid of sp. gr. 1·5 with 2 parts by weight of pure concentrated sulphuric acid of sp. gr. 1·845 is prepared, and allowed to cool in a closed vessel, and 375 g. of this mixture are weighed into a beaker of about 500 c.c. capacity; a thermometer which serves as a stirrer during the nitration is introduced, and the beaker is placed in a capacious vessel of cold water. The water is kept circulating by

[1] Lewkowitsch, *Chem. Zeit.,* 1895, 19, 1423.

passing it through a stout rubber tube carefully laid on to the sides of the cooling vessel. The water is allowed to run away by overflowing the vessel. It should be carefully noted that the rubber tube must be securely attached to the tap if the nitration is carried on near the water-supply tap, as it may easily happen that it is thrown off the tap owing to a sudden alteration of pressure in the supply pipe. If any water is thrown into the nitration mixture, the temperature may easily rise to danger point. The safest plan is therefore to use a thin-walled beaker, so that in case of emergency the thermometer may be quickly pushed through the bottom.

When the temperature of the acid mixture has fallen to 12°-15°, 50 g. of the dynamite glycerin to be tested is weighed out into a lipped beaker and allowed to fall, drop by drop, into the acid, whilst continually stirring with the thermometer. The temperature should be read after the addition of each drop. As this operation is not without danger, it is best for an unpractised experimenter to have the process demonstrated to him. If this be impossible the nitration should be performed very slowly and exactly as described, that is, with continual stirring to avoid any local overheating, taking care that no further glycerin be added, until the temperature has fallen to 25°. A temperature of 30° must never be exceeded. A practised operator will, of course, proceed much more quickly.

When all the glycerin has been introduced the stirring is continued until the temperature falls to 15°. The mixture of nitroglycerin and acids is then transferred to a perfectly dry separating funnel. (It is best to rinse out the separator with concentrated sulphuric acid beforehand.)

If the glycerin is of good quality, the nitroglycerin separates quickly, floating on the acid as an oily, somewhat turbid layer. The more rapidly the separation into two layers with a sharply defined dividing line takes place, the better is the glycerin. If slimy or flocculent particles remain suspended in the nitroglycerin, or the separation is incomplete after five to ten minutes, or if the dividing line is indistinct in consequence of a cloudy intermediate layer, the glycerin is unsuitable for the manufacture of nitroglycerin.

In the case of a very bad glycerin no separating line at all can be observed, and the nitroglycerin appears honeycombed with cellular matter which separates out only after many hours' standing. Such a glycerin must of course be rejected.

In consequence of the danger attending this test, it has been proposed to reduce the quantity of glycerin taken for the determination to 15 g. This should, however, be the lowest permissible limit, as the results of the nitration become absolutely unreliable when as little as 10 g. are taken.

Table 35.

Specific Gravities of Aqueous Solutions of Chemically pure Glycerin.

Glycerol. Per cent.	Lenz. Sp. gr. at 12° to 14°C. Water at 12°=1.	Strohmer. Sp. gr. at 17°·5 C. Water at 17°·5=1.	Gerlach. Sp. gr. at 15°C. Water at 15°=1.	Gerlach. Sp. gr. at 20°C. Water at 20°=1.	Nicol. Sp. gr. at 20°C. Water at 20°=1.
100	1·2691	1·262	1·2653	1·2620	1·26348
99	1·2664	1·259	1·2628	1·2594	1·26091
98	1·2637	1·257	1·2602	1·2568	1·25832
97	1·2610	1·254	1·2577	1·2542	1·25572
96	1·2584	1·252	1·2552	1·2516	1·25312
95	1·2557	1·249	1·2526	1·2490	1·25052
94	1·2531	1·246	1·2501	1·2464	1·24790
93	1·2504	1·244	1·2476	1·2438	1·24526
92	1·2478	1·241	1·2451	1·2412	1·24259
91	1·2451	1·239	1·2425	1·2386	1·23990
90	1·2425	1·236	1·2400	1·2360	1·23720
89	1·2398	1·233	1·2373	1·2333	1·23449
88	1·2372	1·231	1·2346	1·2306	1·23178
87	1·2345	1·228	1·2319	1·2279	1·22907
86	1·2318	1·226	1·2292	1·2252	1·22636
85	1·2292	1·223	1·2265	1·2225	1·22365
84	1·2265	1·220	1·2238	1·2198	1·22094
83	1·2238	1·218	1·2211	1·2171	1·21823
82	1·2212	1·215	1·2184	1·2144	1·21552
81	1·2185	1·213	1·2157	1·2117	1·21281
80	1·2159	1·210	1·2130	1·2090	1·21010
79	1·2122	1·207	1·2102	1·2063	1·20739
78	1·2106	1·204	1·2074	1·2036	1·20468
77	1·2079	1·202	1·2046	1·2009	1·20197
76	1·2042	1·199	1·2018	1·1982	1·19925
75	1·2016	1·196	1·1990	1·1955	1·19653
74	1·1999	1·193	1·1962	1·1928	1·19381
73	1·1973	1·190	1·1934	1·1901	1·19109
72	1·1945	1·188	1·1906	1·1874	1·18837
71	1·1918	1·185	1·1878	1·1847	1·18565
70	1·1889	1·182	1·1850	1·1820	1·18293
69	1·1858	1·179	...	...	1·18020
68	1·1826	1·176	...	...	1·17747
67	1·1795	1·173	...	...	1·17474
66	1·1764	1·170	...	...	1·17201
65	1·1733	1·167	1·1711	1·1685	1·16928
64	1·1702	1·163	...	...	1·16654
63	1·1671	1·160	...	...	1·16380
62	1·1640	1·157	...	...	1·16107
61	1·1610	1·154	...	...	1·15834
60	1·1582	1·151	1·1570	1·1550	1·15561
59	1·1556	1·149	...	...	1·15288
58	1·1530	1·146	...	...	1·15015
57	1·1505	1·144	...	...	1·14742
56	1·1480	1·142	...	...	1·14469
55	1·1455	1·140	1·1430	1·1415	1·14196
54	1·1430	1·137	...	...	1·13923
53	1·1403	1·135	...	...	1·13650
52	1·1375	1·133	...	...	1·13377
51	1·1348	1·130	...	...	1·13104
50	1·1320	1·128	1·1290	1·1280	1·12831
45	1·1183	...	1·1155	1·1145	1·11469
40	1·1045	...	1·1020	1·1010	1·10118
35	1·0907	...	1·0885	1·0875	1·08786
30	1·0771	...	1·0750	1·0740	1·07469
25	1·0635	...	1·0620	1·0610	1·06166
20	1·0498	...	1·0490	1·0480	1·04884
15	1·0374	...	...	...	1·03622
10	1·0245	...	1·0245	1·0235	1·02391
5	1·0123	...	...	...	1·01184
0	1·0000	...	1·0000	1·0000	1·00000

3. CHEMICALLY PURE GLYCERIN.

This glycerin forms the purest commercial product, and should—except for the presence of a small proportion of water—represent the chemical compound, $C_3H_8O_3$, *i.e.* glycerol. In commerce the following qualities are recognised :—

Chemically pure glycerin of sp. gr. .	.	.	1·24
„ „	.	.	1·25
„ „	.	.	1·26

The percentage is most rapidly determined from the specific gravity in accordance with Table 35, p. 205.

When determining the specific gravity of the most concentrated glycerin, it is of importance to ensure that it is free from air-bubbles. To avoid these it is best to warm the sample in a corked flask until all the bubbles have risen to the top. The flask is then allowed to cool to the ordinary temperature, and the glycerin carefully transferred to a pyknometer by pouring it down the side of the vessel.

Table 36.

The Specific Gravities and Refractive Indices of Aqueous Solutions of Glycerin. (Lenz.)

Anhydrous glycerol.	Sp. gr. at 12° to 14°.	Refractive index at 12°·5 to 12°·8.	Anhydrous glycerol.	Sp. gr. at 12° to 14°.	Refractive index at 12°·5 to 12°·8.	Anhydrous glycerol.	Sp. gr. at 12° to 14°.	Refractive index at 12°·5 to 12°·8	Anhydrous glycerol.	Sp. gr. at 12° to 14°.	Refractive index at 12°·5 to 12°·8.
100	1·2691	1·4758	74	1·1999	1·4380	49	1·1293	1·3993	24	1·0608	1·3639
99	1·2664	1·4744	73	1·1973	1·4366	48	1·1265	1·3979	23	1·0580	1·3626
98	1·2637	1·4729	72	1·1945	1·4352	47	1·1238	1·3964	22	1·0553	1·3612
97	1·2610	1·4715	71	1·1918	1·4337	46	1·1210	1·3950	21	1·0525	1·3599
96	1·2584	1·4700	70	1·1889	1·4321	45	1·1183	1·3935	20	1·0498	1·3585
95	1·2557	1·4686	69	1·1858	1·4304	44	1·1155	1·3921	19	1·0471	1·3572
94	1·2531	1·4671	68	1·1826	1·4286	43	1·1127	1·3906	18	1·0446	1·3559
93	1·2504	1·4657	67	1·1795	1·4267	42	1·1100	1·3890	17	1·0422	1·3546
92	1·2478	1·4642	66	1·1764	1·4249	41	1·1072	1·3875	16	1·0398	1·3533
91	1·2451	1·4628	65	1·1733	1·4231	40	1·1045	1·3860	15	1·0374	1·3520
90	1·2425	1·4613	64	1·1702	1·4213	39	1·1017	1·3844	14	1·0349	1·3507
89	1·2398	1·4598	63	1·1671	1·4195	38	1·0989	1·3829	13	1·0332	1·3494
88	1·2372	1·4584	62	1·1640	1·4176	37	1·0962	1·3813	12	1·0297	1·3480
87	1·2345	1·4569	61	1·1610	1·4158	36	1·0934	1·3789	11	1·0271	1·3467
86	1·2318	1·4555	60	1·1582	1·4140	35	1·0907	1·3785	10	1·0245	1·3454
85	1·2292	1·4540	59	1·1556	1·4126	34	1·0880	1·3772	9	1·0221	1·3442
84	1·2265	1·4525	58	1·1530	1·4114	33	1·0852	1·3758	8	1·0196	1·3430
83	1·2238	1·4511	57	1·1505	1·4102	32	1·0825	1·3745	7	1·0172	1·3417
82	1·2212	1·4496	56	1·1480	1·4091	31	1·0798	1·3732	6	1·0147	1·3405
81	1·2185	1·4482	55	1·1455	1·4079	30	1·0771	1·3719	5	1·0123	1·3392
80	1·2159	1·4467	54	1·1430	1·4065	29	1·0744	1·3706	4	1·0098	1·3380
79	1·2122	1·4453	53	1·1403	1·4051	28	1·0716	1·3692	3	1·0074	1·3367
78	1·2106	1·4438	52	1·1375	1·4036	27	1·0689	1·3679	2	1·0049	1·3355
77	1·2079	1·4424	51	1·1348	1·4022	26	1·0663	1·3666	1	1·0025	1·3342
76	1·2046	1·4409	50	1·1320	1·4007	25	1·0635	1·3652	0	1·0000	1·3330
75	1·2016	1·4395									

The refractive index may also be used to determine the proportion of glycerin. Table 36, p. 206, gives the numbers determined by Lenz.

For exact determinations it is necessary to adhere to the temperatures given, and for this reason Lenz recommends determining the refraction of the glycerin, and then that of pure water, at the same temperature, immediately afterwards; the influence of temperature and of small fluctuations in the adjustment of the scale are thus eliminated.

The differences between the refractive indices of glycerin solutions and of pure water are given in the following Table:—

Table 37.

Differences between the Refractive Indices of Aqueous Solutions of Glycerin and Pure Water. (Lenz.)

n_D glycerol $- n_D$ water.	Per cent. of glycerol by weight.	n_D glycerol. $- n_D$ water.	Per cent. of glycerol by weight.	n_D glycerol. $- n_D$ water.	Per cent. of glycerol by weight.	n_D glycerol. $- n_D$ water.	Per cent. of glycerol by weight.
0·1424	100	0·1046	74	0·0645	48	0·0288	22
0·1410	99	0·1032	73	0·0630	47	0·0275	21
0·1395	98	0·1018	72	0·0616	46	0·0261	20
0·1381	97	0·1003	71	0·0601	45	0·0238	19
0·1366	96	0·0987	70	0·0587	44	0·0225	18
0·1352	95	0·0970	69	0·0572	43	0·0212	17
0·1337	94	0·0952	68	0·0556	42	0·0199	16
0·1323	93	0·0933	67	0·0541	41	0·0186	15
0·1308	92	0·0915	66	0·0526	40	0·0173	14
0·1294	91	0·0897	65	0·0510	39	0·0160	13
0·1279	90	0·0889	64	0·0495	38	0·0146	12
0·1264	89	0·0861	63	0·0479	37	0·0133	11
0·1250	88	0·0842	62	0·0464	36	0·0120	10
0·1235	87	0·0824	61	0·0451	35	0·0108	9
0·1221	86	0·0806	60	0·0438	34	0·0096	8
0·1206	85	0·0792	59	0·0424	33	0·0083	7
0·1191	84	0·0780	58	0·0411	32	0·0071	6
0·1177	83	0·0768	57	0·0398	31	0·0058	5
0·1162	82	0·0757	56	0·0358	30	0·0046	4
0·1148	81	0·0745	55	0·0372	29	0·0033	3
0·1133	80	0·0731	54	0·0385	28	0·0021	2
0·1119	79	0·0717	53	0·0345	27	0·0008	1
0·1104	78	0·0702	52	0·0332	26	0·0000	0
0·1090	77	0·0688	51	0·0318	25		
0·1075	76	0·0663	50	0·0315	24		
0·1061	75	0·0659	49	0·0302	23		

For the determination of the refractive index of dilute glycerin solutions, the "immersion-refractometer" may also be used. It should be noted, however, that this instrument may only be used for solutions containing less than 28 g. of glycerol in 100 c.c. of solution.

In the case of dilute solutions containing chemically pure glycerin, the best method of estimation is oxidation with either bichromate or permanganate. The latter is best carried out by using the modification

of Wanklyn and Fox's process proposed by R. Benedikt and R. Zsigmondy.[1] This depends upon the complete oxidation of the glycerol in cold, strongly alkaline solution to oxalic acid, according to the equation :—

$$C_3H_8O_3 + 3O_2 = C_2H_2O_4 + CO_2 + 3H_2O.$$
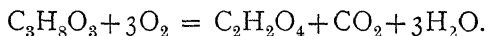
For the test, 0·2-0·3 g. of highly concentrated glycerin or the corresponding quantity of dilute glycerin (calculated approximately from the specific gravity) are placed in a capacious flask and diluted to about 250 c.c. with water. 10 g. of solid potassium hydroxide are added, and then a 5 per cent. solution of potassium permanganate, at the ordinary temperature, until the solution is no longer green but blue or blackish. If preferred, solid, finely powdered potassium permanganate may be added. On heating to boiling, hydrated manganese dioxide separates out, and the liquid becomes red. A solution of sulphurous acid or sodium sulphite is then added until the liquid is just decolorised. The solution is filtered through a smooth filter paper of such a size that it takes at least half of the liquid at once, the filter is carefully washed with hot water, and the filtrate acidified with acetic acid. The last washings are frequently turbid through containing some hydrated manganese dioxide ; this turbidity disappears, however, in the acidification with acetic acid as the liberated sulphurous acid reduces the manganese dioxide. The solution is heated to boiling, and the oxalic acid precipitated by the addition of 10 c.c. of a 10 per cent. solution of calcium chloride. The precipitate of calcium oxalate is further treated in the usual way, and the oxalic acid is calculated to glycerol according to the above equation.

The content of ash plus polyglycerols should not exceed 0·03 per cent. ; the ash itself should not exceed 0·01 per cent.

Acrolein (and other reducing substances) are best detected by the addition of a few drops of silver nitrate solution to the dilute solution of the glycerin, the solution being allowed to stand for twenty-four hours at the ordinary temperature. The test is still more delicate if ammoniacal silver nitrate be used.

Volatile Fatty Acids are recognised by heating the glycerin with alcohol and concentrated sulphuric acid, when ethyl esters of the acids are formed, which can be detected by their odour, recalling that of pine apple.

Sugar is determined polarimetrically.

Arsenic should be entirely absent. A rapid and most sensitive test for arsenic is that of Gutzeit. For this test, 2 c.c. of the sample are introduced into a tall test tube and treated with zinc (free from arsenic) and a few cubic centimetres of absolutely pure dilute sulphuric acid.

[1] *Chem. Zeit.*, 1885, **9**, 975 ; *J. Soc. Chem. Ind.*, 1885, **4**, 610.

The mouth of the test tube is covered with a close-fitting cap of filter paper, two or three layers in thickness, the innermost layer of which has been moistened with a 50 per cent. solution of silver nitrate with the aid of a glass rod. In presence of arsenic, arseniuretted hydrogen is evolved. After standing for ten minutes, the paper cap is taken off. There should be no deep yellow stain on the inner layer of paper. Only a very pale yellow coloration is permissible. This test is so extremely sensitive, that it is absolutely essential to carry out a blank test with the same reagents. This silver nitrate test is almost too sensitive (although commercial glycerins are met with which give no colour after ten minutes), and has been replaced by the less delicate test, in which the silver nitrate solution is replaced by a concentrated solution of mercuric chloride. A glycerin may be considered as practically free from arsenic when no yellow colour is obtained after ten minutes. If mercuric chloride is used, hydrochloride acid may be taken instead of sulphuric; with silver nitrate, hydrochloric acid is not permissible, as small quantities of hydrogen chloride gas may be evolved if the solution becomes warm.

The Marsh-Berzelius test may of course also be used. This is fully described in the section on the " Manufacture of Sulphuric Acid," Vol. i., part i., pp. 363 *et seq.*

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RESINS, BALSAMS, AND GUM-RESINS

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RESINS, balsams, and gum-resins are the secretions of chiefly exotic
plants, and represent mixtures of varying composition. They are used
in industry and in medicine. The methods employed to obtain them
are usually so cumbersome and so crude that the substances which come
on the market as resin, balsam, and gum-resin are completely changed
products, differing widely from their original form as they occur in
nature. Since most of the consignors are non-Europeans, it has been
possible only in the case of a few resins to obtain authentic samples.

On account of the great distances from which the resins come, the
many hands through which they pass, and their completely changed
and varying composition, the examination of samples obtained direct
from the tree, and of authenticated purity, is extremely useful and
of fundamental importance. The analytical data obtained from such
genuine samples, *e.g.* of Peru balsam, have led to definite conclusions,
but have also shown that the commercial article very seldom
corresponds to the genuine resin. A demand for the genuine article
would lead to the rejection of nearly all commercial samples. Hence
in the examination of commercial samples certain variations must be
allowed, and concordant results, such as are obtained in the case of fats
and oils, must not be expected; unfortunately, the analyses of resins
so far published not only vary within wide limits, but are, speaking
generally, actually contradictory. For this reason it is not possible, at
present at any rate, to lay down reliable methods of examination, or
even to fix certain limits within which characteristic values may vary.[1]

As regards classification, the subdivision into resins, balsams, and
gum-resins has been retained, although numerous attempts have been
made to classify these substances on a chemical basis.[2] This sub-
division appears to be the most convenient, especially from the stand-
point of commercial and technical considerations.

The examination of resins comprises both qualitative and quanti-

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[1] *Cf.* K. Dieterich, *Analyse der Harze, Balsame, und Gummiharze nebst ihrer Chemie und Pharmakognosie*, 1900.

[2] *Cf.* A. Tschirsch, *Harze und Harzbehälter.*

tative tests. Whereas formerly qualitative tests, colour reactions, etc., were used almost exclusively for identification and for evaluation, a large number of quantitative tests (to some extent included in the Pharmacopœias) are now available. The most important of these are the determination of the acid and saponification values (and their difference, the ester values), a method of valuation borrowed from the analysis of fats and oils. While the determination of these values furnishes really useful numbers, the iodine-bromine values of the resins are of minor importance. As more recent proposals the following quantitative methods, which may be used to complement the above values, may be mentioned:—The methyl value (Gregor and Bamberger), the carbonyl value (Kitt), the acetyl value (K. Dieterich), and the examination of the resin alcohols and acids (K. Dieterich).

The determinations now generally included in the analysis of resins are :—

(*a*) The Acid Value.

(*b*) The Saponification or Resin Value.

(*c*) The Ester Value (the difference between (*a*) and (*b*).

(*d*) Loss at 100° (Moisture).

(*e*) Ash.

(*f*) Proportion soluble in Alcohol.

(*g*) Proportion insoluble in Alcohol.

(*h*) Specific Gravity.

And the following more special determinations :—

(*i*) Determination of the Cinnamein and Resin Esters in Peru Balsam.

(*k*) Acetyl, Carbonyl, and Methyl Values.

(*l*) Examination of Resin Acids and Alcohols.

(*m*) Qualitative Reactions.

Any single estimation in the case of resins cannot obviously be regarded as conclusive, but the relations of the several data obtained under the above headings often renders it possible to draw certain conclusions.

A.—Methods of Analysis.

The meaning of certain terms, as used in this Section, is as follows :—

The Acid Value.—The number of milligrams of potassium hydroxide required for the neutralisation of the free acid in 1 g. of the resin.

The Acid Value of the Volatile Portions.—The number of milligrams of potassium hydroxide required to neutralise 500 g. of distillate obtained from 0·5 g. of gum-resin by distillation in a current of steam, *e.g.*, in ammoniacum, galbanum.

The Saponification Value.—The number of milligrams of potassium hydroxide required to saponify 1 g. of resin.

The Resin Value.— The number of milligrams of potassium hydroxide required to neutralise 1 g. of (certain) resins and gum-resins on cold fractional saponification with alcoholic potassium hydroxide alone.

The Total Saponification Value (Fractional Saponification).—The total number of milligrams of potassium hydroxide required to neutralise 1 g. of (certain) resins and gum-resins, on cold fractional saponification successively with alcoholic and aqueous potassium hydroxide.

The Gum Value.—The difference between the total saponification value and the resin value.

The Ester Value.—The difference between the acid value and the saponification value.

The Acetyl Value.—The difference between the acetyl saponification value and the acetyl acid value.

The Carbonyl Value.—The percentage of carbonyl oxygen in the resin.

The Methyl Value.—The percentage of methoxyl, calculated as " methyl " (CH_3), obtained from 1 g. of the resin.

The details for the determination of these characteristic values depend on the nature of the substance under examination (see examples); for most resins several alternative methods have hitherto been in use.

(a) The Acid Value.

1. By Direct Titration (A. Kremel).—If the resin is completely soluble in alcohol, chloroform, or benzene-alcohol, the solution of 1 g. of the sample is titrated with $N/2$ or $N/10$ alcoholic potassium hydroxide, phenolphthalein being used as the indicator. If the substance is not completely soluble an alcoholic extract is titrated as above, and the result calculated to 1 g. of the sample. (*Examples :*— Gum-resins, benzoin, storax.) An alternative method is to prepare a water-alcohol extract by heating 1 g. of the finely ground substance with 30 c.c. of water under a reflux condenser, adding 50 c.c. of 96 per cent. alcohol, and boiling again under the reflux condenser for fifteen minutes for each extraction; the extract is allowed to cool and is then titrated without filtering the solution. (*Examples :*—Myrrh, bdellium, opoponax, sagapenum.)

2. By Indirect Titration (K. Dieterich).

(*a*) In the case of completely or almost completely soluble ester-free resins, the alkali simultaneously neutralises the acid and dissolves the resin. 1 g. of the ester-free resin is digested in a glass-stoppered

bottle with 25 c.c. of $N/2$ alcoholic potassium hydroxide solution and 50 c.c. of light petroleum spirit—or benzene in the case of copal—for twenty-four hours; $N/2$ sulphuric acid, with phenolphthalein as the indicator, is used for the titration of the excess of alkali. (*Examples:*— Colophony, dammar, sandarac, mastic, guaiacum, copal.)

(β) In the case of partially soluble resins, containing esters which are saponified with difficulty, when the alkali neutralises the acid and dissolves out the acidic portions. 1 g. of the finely ground resin is digested in a stoppered bottle for twenty-four hours with 10 c.c. of alcoholic, and 10 c.c. of aqueous, $N/2$ potassium hydroxide solution, and the excess of alkali titrated back after addition of 500 c.c. of water. (*Examples:*—Asafœtida, olibanum.)

(γ) In the case of partially soluble resins, containing esters, a water-alcohol extract is used. 1 g. of the finely ground resin is boiled with 50 c.c. of water for fifteen minutes under a reflux condenser; 100 c.c. of strong alcohol are added, the liquid boiled for a further fifteen minutes, allowed to cool, and made up to 150 c.c. To 75 c.c. of the filtrate, equivalent to 0.5 g. substance, are added 10 c.c. of $N/2$ alcoholic potassium hydroxide solution, and after standing in a small flask for exactly five minutes the solution is titrated back with $N/2$ sulphuric acid, using phenolphthalein as indicator. (*Examples:*— Ammoniacum, galbanum.)

(δ) In the case of almost completely soluble resins, containing easily saponifiable esters, the natural product as such is used. The finely ground sample is digested for exactly five minutes with 10 c.c. of $N/2$ alcoholic potassium hydroxide solution. (*Example:*— Benzoin.)

3. **By estimating the Acid Value of the Volatile Acids.**—(For gum-resins containing much essential oil.) A small quantity of water is added to 0.5 g. of the resin in a flask attached to an inclined condenser and heated on a sand-bath (to avoid excessive condensation), and a current of steam passed through. The condenser tube dips into 40 c.c. of $N/2$ potassium hydroxide solution contained in a receiver. When exactly 500 c.c. have passed over, the condenser tube is rinsed with distilled water, and the solution titrated back with standard acid, using phenolphthalein as the indicator. (*Examples:*— Ammoniacum, galbanum.)

(b) The Saponification Value.

1. Determination in the Hot Solution.

(a) 1 g. of a completely soluble resin is boiled for thirty minutes under a reflux condenser with 25-30 c.c. of $N/2$ alcoholic potassium hydroxide, diluted with alcohol and titrated with $N/2$ sulphuric acid, using phenolphthalein as the indicator. (*Examples:*—Almost all balsams and resins.)

If the substance is not completely soluble, either of the two following methods may be used :—

(β) The alcoholic extract is titrated exactly as in (a), and the result calculated on 1 g. of the sample. (*Examples*:—Gum-resins, benzoin, storax.)

(γ) Water is added to the sample to dissolve the gummy portions, and it is then heated as in (a). (*Example*:—Myrrh.)

2. Determination in the Cold Solution (K. Dieterich).

(a) In the case of completely soluble resins 1 g. of the sample is allowed to stand for twenty-four hours at the ordinary temperature in a 500 c.c. stoppered bottle with 50 c.c. of petroleum spirit of sp. gr. 0·700 at 15°, and 50 c.c. of $N/2$ alcoholic potassium hydroxide solution; it is then titrated back with $N/2$ sulphuric acid. To dissolve any salt which may have separated on the bottom of the bottle, which may happen with Peru balsam, 300 c.c. of water are added before titration. (*Examples*:— Peru balsam, copaiba balsam, benzoin, storax.)

(β) In the case of incompletely soluble resins, two portions of 1 g. each are powdered and allowed to stand, with frequent shaking, for twenty-four hours at the ordinary temperature in a 1 litre stoppered bottle with 50 c.c. of petroleum spirit of sp. gr. 0·700 at 15° and 25 c.c. of $N/2$ alcoholic potassium hydroxide solution, added in the order given. One portion is titrated back after addition of 500 c.c. of water with $N/2$ sulphuric acid, using phenolphthalein as the indicator, the liquid being agitated during the titration by imparting a rotary motion to the flask. This gives the "resin value." To the second portion are added 25 c.c. of $N/2$ aqueous potassium hydroxide and 75 c.c. of water; this is allowed to stand, with frequent shaking, for a further twenty-four hours, when 500 c.c. of water are added, and is then titrated with $N/2$ sulphuric acid, with agitation as before. The result obtained is the "total saponification value." The difference is termed the "gum value." (*Examples*:—Ammoniacum, galbanum.)

(c) The Ester Value.

This value is the difference between the acid and the saponification values.

(d) Loss at 100° (Moisture).

For this determination from 2-3 g. of the resin are heated in an oven at 100° to constant weight. Resins containing essential oils lose, of course, volatile substances as well as water. (*Examples*:—All resins except balsams.)

(e) Ash.

This is determined by incinerating the residue obtained in (d).

(f) The proportion Soluble in Alcohol.

The sample is extracted with 90 or 96 per cent. alcohol, either by mixing 10 g. of the sample with sand and extracting in a Soxhlet apparatus, or by dissolving in a flask attached to a reflux condenser, filtering the resulting solution on a tared paper and washing the residue with hot alcohol. The solvent in the filtrate is evaporated off and the residue dried at 100° to constant weight. To avoid creeping during the evaporation, the dish is placed in water in a larger dish, which serves as a water-bath; by adopting this expedient the alcohol never rises above the level of the water outside. In the case of resins containing essential oils, such as gum-resins, it is preferable to estimate the insoluble portion and to calculate from this the soluble portion: the volatile portions, which otherwise might be overlooked, are thus included in the result.

(g) The proportion Insoluble in Alcohol.

The residue from (f) is dried at 100° to constant weight.

Instead of using alcohol for the extraction in (f), and (g), ether, petroleum naphtha, light petroleum spirit, chloroform, etc., may be employed.

(h) Specific Gravity at 15°.

The specific gravity of liquid resins, such as Mecca, Copaiba, and Peru balsams, is determined with the Mohr-Westphal balance, and that of solid resins by the methods used for wax (see p. 107).

For solid resins, such as colophony, salt solutions of known concentration may be used.

(i) Determination of the Cinnameïn and Resin Esters in Peru Balsam.

The estimation of the cinnameïn is best carried out immediately after the determination of the portion soluble in ether (see g above). The ethereal filtrate is shaken out twice successively in a separating funnel with 2 per cent. sodium hydroxide solution, using 20 c.c. each time, washed twice with water and dried for thirty minutes on the water-bath (Thoms).

The determination of the resin esters follows conveniently on the cinnameïn determination, the brown alkaline resin solution from which, after separation from the ethereal liquid, is precipitated with dilute hydrochloric acid. The precipitate is collected on a tared filter and washed on the pump until free from chlorine. The resin is dried at 80° to constant weight and its percentage calculated. (Example:—Peru balsam.)

(*k*) The Acetyl, Carbonyl, and Methyl Values.

1. The Acetyl Value.

The resin is boiled under a reflux condenser with an excess of acetic anhydride and anhydrous sodium acetate either until solution is complete, or until no more dissolves. The solution thus obtained is poured into water, and the separated product collected on a filter and exhausted with boiling water until all free acetic acid has been removed. (The insoluble residues from dammar and copal are similarly treated.) The acetyl products are dissolved in alcohol and the acid and saponification values determined as described in the section on "Oils, Fats, and Waxes," pp. 122 and 114. The difference between the acetyl acid value and the acetyl saponification value is the "acetyl (ester) value." (*Examples :*—Turpentine, colophony, sandarac, dammar, copal.)

2. The Carbonyl Value (M. Kitt).

The substance is warmed with sodium acetate and an accurately measured quantity of phenylhydrazine hydrochloride in dilute alcoholic solution. The excess of phenylhydrazine hydrochloride is ascertained by oxidation with Fehling's solution and measuring the nitrogen evolved. The carbonyl value is found from the formula :—

Percentage of carbonyl oxygen $= V - V_0 \dfrac{0.07178}{S}$ where V is the

volume of nitrogen obtained from the total phenylhydrazine hydrochloride added, and V_0 that of the excess left, both reduced to 0° and 760 mm., and S the weight of substance used. (*Examples :*—Sandarac, elemi, colophony, copal, acaroid.)

3. The Methyl Value (G. Gregor).

This determination is based upon Zeisel's method. The methoxyl groups present are removed as methyl iodide by means of hydriodic acid, and the methyl iodide estimated as silver iodide.[1]

(*l*) Examination of the Resin Acids.

The saponification products of the resins, as obtained above (*b* 1 and *b* 2) are decomposed with acid, washed and dried. The resulting substances are examined both qualitatively and quantitatively by determining their solubility in various solvents, and their acid and saponification (also ester) values. (*Examples :*—Balsams, benzoin, colophony, dammar, copal).

(*m*) Qualitative Reactions.

These are described below under the heading B.

[1] *Cf.* G. Gregor, *Monatsh.*, 1898, **19**, 116 ; *J. Soc. Chem. Ind.*, 1898, **17**, 609.

B.—CHARACTERISTIC VALUES AND STANDARDS OF QUALITY.

The subjoined tabular statement of the characteristic values of resins, balsams, and gum-resins is based on the determinations of Williams, Kremel, von Schmidt and Erban, Gehe and Co., Beckurts and Brüche, E. Dieterich, K. Dieterich, Tschirch, and others. The values, which are given in round numbers, do not constitute a criterion of purity and quality; they are merely intended to show the limits of the numbers, as determined by the several methods of examination employed. The solubilities given represent the demands which present experience justifies. Only the most important balsams, resins, and gum-resins are included in the Tables.

I. BALSAMS.
Copaiba.

		Solubility.	
1. Maracaibo.			
Acid value (by *a*1)*	75 to 100	Ether	⎫
Saponification value (by *b*1*a*)	80 „ 100	Chloroform	⎪ Completely
„ („ *b*2*a*)	80 „ 90	Petroleum spirit	⎬ soluble
Ester value	0·5 „ 8	Oil of turpentine	⎪
Sp. gr.	0·96 „ 0·99	Carbon bisulphide	⎭
Methyl value (by *k*3)	0	Alcohol (90%)	⎫ Only
		Ethyl acetate	⎬ partially soluble
2. Para (Maranham).			
Acid value (by *a*1)	25 to 65	Ether	⎫
Saponification value (by *b*1*a*)	30 „ 70	Chloroform	⎪ Completely
„ („ *b*2*a*)	30 „ 60	Benzene	⎬ soluble
Ester value	2 „ 18	Oil of turpentine	⎭
Sp. gr.	0·91 „ 0·99	Alcohol (90%)	⎫
		Ethyl acetate	⎪ Only
		Petroleum spirit	⎬ partially soluble
		Carbon bisulphide	⎭
3. East Indian (Gurjun Balsam).			
Acid value (by *a*1)	5 to 20	Alcohol (90%)	⎫
Saponification value (by *b*1*a*)	8 „ 20	Chloroform	⎪ Completely
„ („ *b*2*a*)	10 „ 25	Ethyl acetate	⎬ soluble
Ester value	1 „ 15	Benzene	⎭
Sp. gr.	0·955 „ 0·980	Oil of turpentine	⎫
		Ether	⎪ Only
		Petroleum spirit	⎬ partially soluble
		Carbon bisulphide	⎭
4. Peru Balsam.			
Acid value (by *a*1)	40 to 80	Chloroform	⎫ Completely
Saponification value (by *b*1*a*)	220 „ 260	Ethyl acetate	⎬ soluble
„ (., *b*2*a*)	240 „ 270	Alcohol 90%	Almost completely soluble
Ester value	140 „ 200	Ether . 92 to 98%	Soluble
Methyl value (by *k*3)	1·4 „ 22·6	Benzene . 94 „ 98%	„
Cinnamein (by *z*)	60 „ 61%	Petroleum spirit . 66 „ 68%	„
Resin esters (by *z*)	19 „ 28	Oil of turpentine . 85 „ 89%	„
Saponification value of cinnamein (by *b*1*a*)	240	Carbon bisulphide . 86 „ 88%	„
Sp. gr.	1·138 to 1·148		

* The letters and figures refer to the methods given under A (pp 211 *et seq.*).

II. RESINS.

Amber.

		Solubility.	
		Fused.	Natural.
Acid value (by $a1$) .	15 to 35	Alcohol . . . . almost insol.	Almost insol.
Saponification value		Ether . . . . partially sol.	,,
(by $b1\beta$) . . .	86 ,, 145	Methyl alcohol . . almost insol.	,,
Ester value . . .	71 ,, 91	Amyl alcohol . . partially sol.	,,
Moisture . . .	1%	Benzene . . { almost completely sol. }	,,
Ash	0·2 to 0·3%	Petroleum spirit . . almost insol.	,,
		Acetone . . . ,,	Insol.
		Glacial acetic acid . . partially sol.	,,
		Chloroform . . . ,,	,,
		Carbon bisulphide . { almost completely sol. }	Partially sol.
		Oil of turpentine . { almost completely sol. }	,,

Copal, which may be confounded with amber, is soluble in cajuput oil, while amber is not. On ignition, amber blackens moist lead acetate paper; copal does not. Adulterants and artificial products from colophony are recognised by their solubility in alcohol and their high acid values.

Benzoin.

1. Siam.		2. Sumatra.	
Acid value (by $a1$) . . .	120 to 170	Acid value (by $a1$) . .	95 to 190
,, (,, $a2\delta$) . .	140 ,, 170	,, ,, (,, $a2\delta$) . .	100 ,, 130
Saponification value (by $b1\beta$) .	170 ,, 210	Saponification value (by $b1\beta$) .	155 ,, 270
,, (,, $b2a$) .	220 ,, 240	,, ,, (,, $b2a$) .	180 ,, 230
Ester value	35 ,, 75	Ester value	30 ,, 175
Ash	0·2 ,, 1·5%	Loss at 100°	4 ,, 9%
Methyl value (by $k3$) . .	28·5 ,, 43·5	Ash	0·2 ,, 1·5%
(Should be soluble in alcohol with little residue, at most 5% vegetable tissue.)		Methyl value (by $k3$) . .	13 ,, 25·5
		(Should be soluble to the extent of 70 to 80% in alcohol.)	

Colophony.

		Solubility.	
Acid value (by $a1$)	145 to 180	Alcohol . . .	
,, (,, $a2a$)	145 ,, 185	Oil of turpentine .	
Sp. gr.	1·045 ,, 1·085	Essential oils .	
Loss at 100°	0·0 ,, 0·5%	Acetone . .	
Ash	0·2 ,, 1·2%	Ether . . .	
Acetyl (by $k1$) { Acid value . { Saponification value.	155·82 ,, 155·84 / 251·21 ,, 274·94	Chloroform . .	} Completely soluble
Carbonyl value (by $k2$) . .	0·54 ,, 0·56	Methyl alcohol .	
Methyl value (by $k3$) . . .	0	Amyl alcohol .	
(Its solution in acetic acid gives a fine red coloration with sulphuric acid.)		Ethyl acetate .	
		Benzene . .	
		Carbon bisulphide .	
		Petroleum naphtha .	
		Light petroleum spirit . . .	} Partially soluble

Copal (Zanzibar).

Acid value (by $a1$)	35 to 95
,, (,, $a2a$)	60 ,, 65
Loss at 100°	0·5 ,, 2·5%
Ash	0·25 ,, 2·0%
Acetyl (by $k1$) { Acid value . . .	77·1 } on the soluble
{ Saponification value . .	203·29 } portion
,, (,, $k1$) { Acid value . . .	210·10 to 221·14 } on the insoluble
{ Saponification value . .	203·94 ,, 231·27 } portion
Carbonyl value (by $k2$)	0·61

Solubility.		
	Natural.	Shelled.
Alcohol	Insoluble	Almost soluble
Ether	Partially soluble	Partially soluble
Methyl alcohol	Insoluble	Insoluble
Amyl alcohol	Slightly soluble	Partially soluble
Benzene	Partially soluble	Almost completely soluble
Petroleum spirit	Insoluble	Insoluble
Acetone	,,	Almost soluble
Glacial acetic acid	Partially soluble	Partially soluble
Chloroform	,,	,,
Carbon bisulphide	Insoluble	Almost soluble
Oil of turpentine	Partially soluble	,,
Cajuput oil	Completely soluble	Completely soluble
Chloral hydrate (80% solution) . . .	Quite insoluble	Quite insoluble

Dammar.

Acid value (by $a1$)	20 to 35
,, (,, $a2a$)	20 ,, 30
Loss at 100°	0·1 ,, 1%
Ash	0·01 ,, 0·1%
Acetyl (by $k1$) { Acid value . . .	50·52 ,, 51·80
{ Saponification value . .	132·08 ,, 134·86

Guaiacum.

		Solubility.	
Acid value (by $a1$) . . .	20 to 45	Alcohol . at least 80%	⎫
,, (,, $a2a$) . .	70 ,, 97	Water . . . 3 to 5%	
Ash	2-10%	Petroleum spirit 0·06 ,, 10%	⎬ Soluble
Acetyl (by $k1$) { Acid value .	13 to 23	Ether . . . 22 ,, 91%	
{ Sap. value .	163 ,, 193	Benzene . . 20 ,, 90%	
Methyl value (by $k3$) . .	73 ,, 84	Carbon bisulphide 12 ,, 37%	⎭
		Chloral hydrate (60 and 80%	⎱ Almost
		solutions)	⎰ completely soluble

Mastic (Levant).

		Solubility.	
Acid value (by $a1$) . . .	50 to 70	Alcohol	Partially sol.
„ („ $a2a$)	44 „ 66	Ether	Soluble
Loss at 100° . . .	0·9 „ 1·5%	Methyl alcohol . . .	Partially sol.
Ash	0·1 „ 0·2%	Amyl alcohol . . .	Soluble
Methyl value (by $k3$) . .	0 „ 1·9	Benzene	„
		Petroleum spirit . . .	Insoluble
		Acetone . . .	Partially sol.
		Glacial acetic acid . .	„
		Chloroform . . .	„
		Carbon bisulphide . .	Slightly sol.
		Oil of turpentine . . .	Partially sol.
		Chloral hydrate (60 to 80% solution)	„

Pine Resin.

		Solubility.	
Acid value (by $a1$) . . .	100 to 160	Alcohol (90%) . . .	Completely sol.
Saponification value (by $b1a$) .	150 „ 190	Chloroform	„
Ester value	10 „ 30	Ethyl acetate . . .	„
Loss at 100°	5 to 12·5%	Benzene	„
Ash	1%	Carbon bisulphide . .	„
Acetyl (by $k1$) { Acid value .	155·27 to 158·48	Ether	„
{ Sap. value .	222·86 „ 230·75	Oil of turpentine . .	Partially sol.
		Petroleum spirit . .	„

Sandarac.

		Solubility.	
Acid value (by $a1$) . . .	95 to 155	Absolute alcohol . .	Completely sol.
„ (by $a2a$) . .	130 „ 160	Ether	„
Loss at 100°	0·04 „ 0·2%	Amyl alcohol . . .	„
Ash	0·1 „ 2%	Methyl alcohol . .	Partially sol.
Acetyl (by $k1$) { Acid value .	166 „ 170	Acetone . . .	Completely sol.
{ Sap. value .	239 „ 252	Chloroform . . .	Partially sol.
Carbonyl value (by $k2$) . .	0·43 „ 0·74	Essential oils . . .	„
		Benzene	Almost insol.
		Glacial acetic acid . .	Partially sol.
		Carbon bisulphide . .	Almost insol.
		Chloral hydrate (60% solution) . . .	{ Almost completely insol.
		Petroleum spirit . .	Partially sol.

Australian samples are more soluble in petroleum spirit than the above African sandarac.

Storax.

		Solubility.
Acid value (by $a1$) . . .	35 to 180	Alcohol . . . . ⎰ Almost com-
Saponification value (by $b1\beta$) .	130 ,, 250	Ethyl acetate . . . ⎱ pletely sol.
,, (,, $b1a$) .	100 ,, 190	Chloroform . . . Partially sol.
Ester value	70 ,, 185	Ether . . . . ,,
Loss at 100° . . .	5 ,, 40%	Benzene . . . . ,,
Ash	0·0 ,, 1·5%	Oil of turpentine . . ,,
Methyl value (by $k3$) . .	3·6 ,, 4·5	Carbon bisulphide . . ,,
		Petroleum spirit . . ,,

Turpentine.

		Solubility.
1. Ordinary Turpen- **tine.**		
Acid value (by $a1$) . . .	110 to 145	Alcohol (90 %) . . Completely sol.
Saponification value ($b1a$) .	108 ,, 180	Ether . . . . ,,
Ester value . . .	2 ,, 60	Chloroform . . . ,,
Acetyl (by $k1$) ⎰Acid value .	123 ,, 126	Ethyl acetate . . . ,,
⎱Sap. value .	187 ,, 217	Benzene . . . . ,,
Carbonyl value (by $k2$) .	0·28 ,, 0·57	Oil of turpentine . . ,,
(This turpentine hardens with calcium hydroxide.)		Carbon bisulphide . . ⎰ Almost com- ⎱ pletely sol.
		Petroleum spirit . . Partially sol.
2. Larch Turpentine.		
Acid value (by $a1$) . .	65 to 100	Alcohol . . . . Soluble
Saponification value (by $b1a$) .	85 ,, 130	Ether . . . . ,,
Ester value	0 ,, 55	Methyl alcohol . . ,,
Acetyl (by $k1$) ⎰Acid value .	70 ,, 72	Amyl alcohol . . . ,,
⎱Sap. value .	179 ,, 191	Benzene . . . . ,,
(This turpentine does not harden with calcium hy-droxide.)		Petroleum spirit . . ⎰ Almost com- ⎱ pletely sol.
		Acetone . . . . Soluble
		Glacial acetic acid . . ,,
		Chloroform . . . ,,
		Ethyl acetate . . . ,,
		Carbon bisulphide . . ⎰ Almost com- ⎱ pletely sol.
		Oil of turpentine . . Completely sol.

III. GUM RESINS.
Ammoniacum.

		Solubility.
Acid value (by $a1$) . .	55 to 135	Partially soluble in all indifferent sol-vents. Alcohol dissolves 90%, water up to 20%. Galbanum is tested for by boiling 5 g. of the ammoniacum, as finely divided as possible, in a dish with 15 g. hydrochloric acid (sp. gr. 1·19) for fifteen minutes, filtering through a double moistened filter, and carefully adding to the clear filtrate an excess of ammonia. The presence of galbanum is shown by the characteristic blue fluorescence of umbelhferon in reflected light.
,, (,, $a3$) . .	100 ,, 200	
,, (,, $a2\gamma$) . .	80 ,, 105	
Saponification value (by $b1\beta$) .	145 ,, 235	
Total sap. value (by $b2\beta$)	99 ,, 155	
Ester value . . .	60 ,, 100	
Resin value . . .	145 ,, 162	
Loss at 100° . . .	2·0 ,, 15%	
Ash	1 ,, 7·5%	
Methyl value (by $k3$) . .	8·6 ,, 11	

Galbanum.

		Solubility.
Acid value (by $a1$) . . .	5 to 70	As for ammoniacum. Ash not to exceed
„ („ $a3$) . . .	72 „ 115	10%.
„ („ $a2\gamma$) . .	20 „ 70	
Saponification value (by $b1\beta$) .	75 „ 245	
Total sap. value (by $b2\beta$) .	107 „ 123	
Ester value	50 „ 180	
Resin value	115 „ 136	
Loss at 100° . . .	1 „ 31%	
Ash	1 „ 30%	
Methyl value (by $k3$) . .	3·7	

Myrrh.

		Solubility.
Acid value (by $a1$) . . .	60 to 70	Partially soluble in all indifferent
Saponification value (by $b1\beta$) .	159 „ 216	solvents. Water should not extract more
„ („ $b1\gamma$) .	220 „ 230	than 50%, and alcohol not less than
Ester value	95 „ 145	35%. Ash not to exceed 7%.
Ash	1 „ 10%	
Methyl value (by $k3$) . .	3·6 „ 4·5	

Olibanum.

Acid value (by $a1$)	45 to 60
„ (by $a2\beta$)	30 „ 50
Saponification value (by $b1\beta$) . . .	65 „ 120
„ („ $b1\gamma$) . . .	110 „ 120
Ester value	6 „ 60
Carbonyl value (by $k2$) . . .	0·36
Methyl value (by $k3$) . . .	5·3 to 6·4

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DRUGS AND GÁLENICAL PREPARATIONS

By K. DIETERICH, Ph.D., Lecturer on Pharmaceutical Chemistry, The Royal
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DRUGS are generally considered to comprise all those crude products
which represent either the dried parts of plants or plant extracts, and
which serve as initial material for the manufacture of various important
pharmaceutical or medicinal preparations. The fact that drugs, to a
large extent, only come into the hands of the manufacturer as
secondary or even more completely altered products, is due to the
chemical changes[1] which always take place in connection with their
production, whether these changes be unintentional or otherwise. As
a result, even with consideration of differences in the character of the
soil, drugs always vary in composition, and methods for their examina-
tion and valuation have therefore become necessary. The standards
resulting from such methods of examination, as in the case of the
resins, can, however, only be expressed by figures denoting the maximum
and minimum limits; for although pharmaco-chemistry has made
great progress, we do not know as yet the constituents, either active or
inactive, of many drugs, to say nothing of being able to determine
their active principles quantitatively. Even with such drugs as contain
alkaloids that are known and can be quantitatively determined, it must
be taken into consideration that the presence, for example, of a certain
proportion of alkaloid does not always afford a guarantee for the good
quality and purity of the drug. The conditions with regard to the
galenical preparations made from the drugs are similar, but for these
many other analytical factors have become available as the result of
experience.

Drugs in a more extended sense, that is, those which are not of
vegetable origin, and also those drugs and preparations for which
complete quantitative tests are given in the Pharmacopœia, have not
been included in this account of the subject. Furthermore, other
drugs have been excluded which are more correctly designated as crude

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[1] *Cf.* K. Dieterich, "On the chemical changes in the production of Drugs," *Helfenberger
Annalen*, 1896, pp. 9-20.

products, such as the fats, oils, waxes, paraffins, and ceresins, since they are dealt with in other Sections.

In view of the large number of drugs which are now technically utilised on a large scale, and the limitations of space, it has naturally only been possible to include here the more important. The present standards of value and the requirements are in accordance with experience, and such as are recorded in the numerous works on pharmaceutical chemistry and pharmaco-chemistry.

A.—DRUGS.

GAMBIR.

PALE CATECHU. CATECHU PALLIDUM. TERRA JAPONICA.

An extract prepared from the leaves and twigs of *Ourouparia Gambir* (Hunter), Baillon.

Gambir and Catechu are frequently confused, but, although similar in character, they are recognised in commerce as distinct products and are obtained from totally different botanical sources. The British Pharmacopœia under the title of Catechu recognises the above-defined product, to which the United States Pharmacopœia gives the title of Gambir. The fourth edition of the German Pharmacopœia included both of the above-mentioned products under the title of Catechu, but in the present edition the term is restricted to the so-called Black Catechu or Cutch.

(a) *Reaction for Identity* (according to K. Dieterich).—If to 3 g. of gambir there be added 25 c.c. of $N/1$ aqueous potassium hydroxide and 50 c.c. of light petroleum (sp. gr. 0·700 at 15°), and the whole shaken a few times in a glass separating funnel, after the separation of the two layers the light petroleum will show in reflected light a green fluorescence, increasing in intensity according to the time of action of the alkali (gambir-fluorescin).

If to the dilute alcoholic solution a solution of ferric chloride be added, an intense green coloration will be produced, which persists for some time.

(b) *Plant Residues.*—If 20 parts of gambir be extracted with 200 parts of boiling alcohol, the insoluble residue, dried at 100°, should amount to not more than 6 parts, or 30 per cent.

(c) *Determination of Ash.*—1 g. of gambir is carefully incinerated, and the residue heated until, after cooling in a desiccator, a constant weight is obtained. Both the British and United States Pharmacopœias require that gambir should yield not more than 5 per cent. of ash.

PEGU CATECHU.

BLACK CATECHU. CATECHU NIGRUM. CUTCH.

An extract prepared from the heartwood of *Acacia Catechu* (Linné fil.), Willdenow.

The following methods of examination and requirements are those of K. Dieterich and of the German Pharmacopœia :—

(a) *Reaction for Identity.*—If to a solution of Pegu catechu in dilute alcohol a solution of ferric chloride be added, a green coloration ensues which quickly changes to brown, and a precipitate is formed which gives a bluish-violet colour with alkalis.

Pegu catechu does not give the fluorescence reaction of gambir.

(b) *Plant Residues.*—The plant residues, determined by the method given under gambir, should not exceed 30 per cent.

(c) *Determination of Ash.*—If this determination be conducted as given under gambir, Pegu catechu should yield not more than 6 per cent. of ash.

ERGOT.

ERGOTA. SECALE CORNUTUM.

(a) *Determination of Extract.*—To 10 g. of the finely crushed drug 100 c.c. of water are added, and the mixture allowed to stand for twenty-four hours in a closed vessel. 20 c.c. of the filtered liquid are then evaporated in a tared porcelain dish to dryness, and the residue heated at 100° until the weight is constant. The weight of dry extract, multiplied by fifty, expresses the percentage of water-soluble extract yielded by the drug.

(b) *Determination of Alkaloid* (according to C. C. Keller).—25 g. of dry powdered ergot are extracted in a glass percolator with light petroleum. When nothing more is removed by this solvent, the drug is dried at a gentle heat, and brought into a tared, dry flask of 250 c.c. capacity. To the powder 100 g. of ether are added, and, after ten minutes, milk of magnesia, prepared by mixing 1 g. of calcined magnesia with 20 c.c. of water. The whole is shaken continuously and vigorously until the ergot has agglomerated and the liquid becomes clear. The shaking is then frequently repeated for half an hour, after which 80 g. of the ethereal liquid, representing 20 g. of the drug, are decanted. This solution is shaken three times in a separator with 25, 15, and 10 c.c. respectively of 0.5 per cent. hydrochloric acid. If the extraction is not then complete, the liquid is shaken once or twice more with 10 c.c. of 0.5 per cent. acid. The acid solution is shaken with an equal volume of ether and an excess of ammonia, and this extraction repeated twice with less ether. The ethereal liquids are united, transferred to a tared flask, and the solvent removed. After

III P

treating the residue twice with a little ether, and evaporating the latter, the flask with its contents is finally dried and weighed. The weight of dry residue, multiplied by five, expresses the percentage of alkaloid present in the ergot.

The following minimum and maximum values have been obtained :—

Extract . . . 12·50 to 17·84 per cent.
Alkaloid . . . 0·10 „ 0·34 „

Requirements.—Ergot has an oily, unpleasant taste, and when mixed with 10 parts of hot water should develop the odour peculiar to it, but this should be neither ammoniacal nor rancid. It should yield the largest possible amount of extract and of alkaloid.[1]

ISINGLASS.

ICHTHYOCOLLA. COLLA PISCIUM.
(*According to K. Dieterich.*)

(a) *Preparation of the Material.*—The kinds of isinglass which are capable of being divided into small pieces by means of shears, or a knife, etc., are cut into strips ½ cm. in width, and these again into squares of ½ cm. When the isinglass is very hard and cannot be divided in this manner, it is best ground in a mill to a powder, which, however, should be as coarse as possible, as the production of a fine powder renders the subsequent operation of filtering extremely difficult.

(b) *Determination of the Moisture.*—About 5 g. of the isinglass, divided into small pieces as described above, is heated in a drying oven at 100°-105° until the weight is constant.

(c) *Determination of the Ash.*—The perfectly dried isinglass remaining from the determination of the moisture is heated by a small flame in a fume chamber having a good draught until the material ceases to emit dense vapours, which have the smell of burnt horn, and there is no longer a strong intumescence. All possible care should also be taken that the isinglass does not burn on to the vessel, so that after a while a brownish black carbonaceous mass remains which is somewhat readily combustible. By the application then of a larger flame, and eventually moistening the material once with water, it may completely and quickly be reduced to a light brown ash.

(d) *Determination of Potassium Carbonate in the Ash.*—The ignited residue obtained by the determination of the ash is taken up with hot water, transferred to a small filter, and washed with about 75-100 c.c. of boiling, distilled water. The filtrate, after the addition of a

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[1] For recent investigations concerning the alkaloids of ergot cf. *J. Chem. Soc.*, 1907, **91**, 337 ; 1909, **95**, 1123 ; 1910, **97**, 284, 2592 ; 1911, **99**, 2336 ; *J. Pharm. Chim.*, 1909 [vi.], **30**, 145.

little tropæolin or methyl orange, is titrated with $N/10$ hydrochloric acid, and the amount of potassium carbonate calculated either on the original substance or on 100 parts of ash.

(e) *Determination of the portions soluble and insoluble in Boiling Water.*—10 g. of the finely divided isinglass are placed in a tall enamelled vessel, preferably an internally enamelled litre measure, with a spout, since glass beakers cannot be used for this purpose. About 500 c.c. of water are then added, and the mixture kept in a steam-bath or water-bath until the isinglass floats for the most part on the surface, so that it cannot burn on to the bottom of.the vessel by the subsequent treatment. It is then heated to boiling over a free flame, and the boiling continued until the intense frothing has ceased or abated. During the evaporation the froth, mixed with the impurities contained in the isinglass, is firmly deposited on the sides of the vessel. At this stage 400 c.c. of hot distilled water are added, and the liquid evaporated to about 300 c.c. Pieces of the isinglass which may adhere to the sides of the vessel are detached from time to time by means of a glass rod, and brought into the boiling liquid. The vessel is then removed from the burner, placed on a steam-bath, and the solid material allowed to deposit, after which the liquid is decanted as completely as possible into a graduated litre flask. About 800 g. of boiling water are then added, the mixture again heated over a free flame, and then evaporated to about 200 c.c., after which it is allowed to deposit, and the liquid decanted as before. This operation is repeated altogether three or four times, until the litre flask is about nine-tenths filled. The flask, especially during warm weather, should be kept hot on a steam-bath or water-bath during the entire procedure, in order to prevent the solution from spoiling. The vessel employed for heating is cleaned from all adhering particles of isinglass by means of a glass rod over which a piece of rubber tubing is drawn, and a little water, and the entire residue finally washed into the litre flask. The contents of the flask are then cooled to 15°, filled up to the mark, and the whole thoroughly shaken and filtered. 50-100 c.c. of the filtrate, which is more or less opalescent, are evaporated in a tared dish, the residue dried at 100°-105° until the weight is constant, and calculated for the percentage of substance soluble in boiling water. The sum of this percentage and that of the moisture, subtracted from 100, gives the percentage of substance contained in the isinglass which is insoluble in boiling water.

(f) *Swelling Value and Gelatinising Power.*—To determine the swelling value 10 g. of the isinglass are placed in a tared, enamelled litre measure, 800 c.c. of hot water added, and, together with a glass rod which is weighed at the same time, the mixture evaporated on a steam-bath, with frequent stirring, to a total weight of about 510 g. If

gelatinisation does not ensue, when completely cold, an additional 50-100 g. of water are evaporated, and it is again allowed to cool. When the point is thus determined at which a jelly is formed, the whole is weighed. If, for example, the weight is found to be 370 g., the gelatinising power is 1 : 36, or the swelling value is 36.

Since it has been found by experience that the gelatinising power is affected by heating over a free flame to boiling and subsequent evaporation, a steam-bath should be employed so that the temperature does not exceed 100°.

(g) *Determination of the Fat.*—10 g. of the finely divided isinglass are weighed into an extraction thimble, placed in a Soxhlet apparatus, and extracted for three hours with ether of sp. gr. 0·720. The contents of the extraction flask are then evaporated, and dried for a short time at 100° until the weight is constant, the weight of the flask itself having been previously determined. The contents of the extraction thimble are also dried, and, after all the ether has evaporated, used for the determination of the glutin.

(h) *Determination of the Collagen.*—The combined weights of the soluble and insoluble portions, minus the fat, expresses the amount of collagen

(i) *Determination of the Crude Glutin.*—The dried contents of the extraction thimble, remaining from the determination of the fat, contains the so-called collagen, that is, the pure gelatin-yielding tissue freed from fat, and this is used for the determination of the glutin as follows :—The contents of the thimble are completely extracted with boiling water, in the same manner as described for determining the portion of the isinglass soluble in boiling water (cf. *e*). 500 c.c. of the filtrate which is finally obtained, corresponding to 5 g. of the isinglass deprived of fat, *i.e.* collagen, are placed in an accurately weighed beaker, and evaporated to about 50 c.c. To the solution, while still warm, 200-300 c.c. of absolute alcohol are gradually added in a thin stream, and the precipitate thus produced allowed to stand for at least twelve hours, or until the supernatant liquid has become perfectly clear. Although the glutin is usually precipitated as an extremely viscid, white mass, opalescent on the surface, it is best to bring the mixture on to a small, weighed filter. The filtrate, together with the alcohol used for washing the glutin and the filter, are then evaporated in a tared dish, the residue being finally dried and weighed (extractive matter not precipitable by alcohol).

It may be noted that in the technical preparation of glutin the isinglass is usually treated with dilute hydrochloric acid before being deprived of fat, in order to remove inorganic constituents. This procedure cannot be adopted in the quantitative determination of glutin, for the reason that other constituents would be dissolved

together with the inorganic substances, and the action of hydrochloric acid is too strong for analytical purposes. If it is desired to ascertain the nature of the small amount of inorganic matter present, the ash yielded by the glutin is determined.

(k) *Determination of the Acid Value.*—If the filtrate obtained by the determination of the soluble portion of the isinglass, when tested with sensitive litmus paper, gives a distinctly acid reaction, the acid value of the solution may be ascertained as follows :—2 g. of isinglass, together with 100-150 c.c. of distilled water, are placed in a flask of 200 c.c. capacity, the liquid heated for about three hours on a steam-bath, then brought once to boiling over an open flame, allowed to cool, filled up to the mark, and filtered after being well shaken. 50 c.c. of the filtrate are finally titrated with $N/10$ aqueous potassium hydroxide, using phenolphthalein as the indicator.

(l) *Determination of the Iodine Value.*[1]—Since isinglass belongs to the albuminoids, or albumen-like substances, its property of absorbing iodine may be used for its identification and the detection of adulterations, as in the case of albumen itself. The determination of the iodine value may be carried out as follows :—50 c.c. of the same filtrate as that employed for the determination of the acid value or of the filtrate used for determining the soluble portion of the isinglass, representing 0.5 g. of the latter, are mixed with 20 c.c. of an $N/10$ solution of iodine in potassium iodide in a glass-stoppered bottle of 500-750 c.c. capacity. The mixture is then well shaken, allowed to stand for twenty-four hours, and the excess of iodine titrated back with $N/10$ sodium thiosulphate, using starch as an indicator. The number of c.c. of $N/10$ iodine solution used, multiplied by 0.012697 and 200 respectively, gives the iodine value of the sample.

(m) *Test for Sulphur.*—The test for sulphur is important, inasmuch as isinglass is often artificially bleached with sulphurous acid, and such a product is generally not so good as that obtained by natural methods. The test consists in fusing the isinglass with a mixture of potassium nitrate and sodium carbonate, and testing the aqueous extract of the fused mass for sulphate in the usual manner.

(n) *Test for Starch.*—The test for starch may also serve as one for identity, since pure isinglass gives no reaction for starch, whereas artificial products may do so. To the aqueous solution a little solution of iodine in potassium iodide is added, when pure isinglass will show a reddish-brown, but no blue coloration.

(o) *Determination of the Optical Rotation of the Glutin Solution.*— The aqueous glutin solution is lævo-rotatory, and the optical rotation is therefore also to be determined as proof of identity of a natural isinglass.

[1] *Cf.* K. Dieterich, *Helfenberger Annalen,* 1897, pp. 1-29.

Table 38.

Analytical Values for Isinglass (K. Dieterich).

(Expressed in round numbers.)

	Russian: Saliansky, Beluga, Samovy.	Chinese.	American: Brazilian, Venezuelan, Maracaibo, and scraps.	Adulterated Saliansky, impregnated with glue.
Moisture	13 to 20 p. c.	11 to 17 p. c.	13 to 18 p. c.	16 p. c.
Ash	0·5 to 1·7 p. c.	0·9 to 2·3 p. c.	1 to 3·7 p. c.	0·6 p. c.
Potassium carbonate in 100 parts of ash .	8 to 33 p. c.	32 to 53 p. c.	6 to 37 p. c.	72 p. c. !
Soluble portion . .	65 to 81 p. c.	68 to 86 p c.	59 to 75 p. c.	82 p. c.
Insoluble portion . .	1 to 19 p c.	2 to 15 p. c.	9 to 25 p. c.	1·5 p. c.
Swelling value . . .	6 to 49	14 to 25	16 to 55	25
Fat	0·1 to 1·2 p. c.	0·1 to 1·2 p. c.	0·1 to 0·8 p. c.	0·3 p. c.
Collagen	79 to 85 p. c.	81 to 88 p. c.	80 to 87 p. c.	83 p. c. !
Crude glutin . . .	66 to 82 p c.	69 to 74 p. c.	66 to 75 p. c.	82 p. c. !
Acid value . . .	0 to 6·0	0	0 to 2·76	3·8 p. c. !
Iodine value . . .	19 to 45	39 to 46	30 to 47	37
Ash of crude glutin . .	0·4 to 0·7 p. c.	0·67 p. c.	0·4 to 0·7 p. c.	0·4 to 0·7 p. c.
Optical rotation of crude glutin . . .	lævo	lævo	lævo	lævo
Test for sulphur . .	positive	positive	positive	positive

OPIUM.

(According to K. Dieterich and the German Pharmacopœia.)

(a) *Determination of Moisture.*—2 g. of the opium are heated in a drying oven at 100° until the weight is constant.

(b) *Determination of Ash.*—The dried opium is incinerated, and the residue ignited until the weight remains constant.

(c) *Determination of Morphine.*—The following method is that of the German Pharmacopœia:—7 g. of opium, dried at 60° and in moderately fine powder, are triturated with 7 g. of water, the mixture being then washed with water into a flask and the total weight made up to 63 g. by the further addition of water. After having stood for an hour with frequent shaking, the mixture is transferred to a dry, folded filter of 10 cm. diameter. To 42 g. of the filtrate (=4·88 g. opium) there is then added 2 c.c. of a mixture of 17 g. solution of ammonia (sp. gr. 0·960) and 83 g. of water, and the whole filtered immediately through a dry, folded filter into a flask. To 36 g. of the filtrate (=4 g. opium) are then added, with agitation, 10 c.c. of ethyl acetate and another 5 c.c. of the above-mentioned dilute ammoniacal liquid. After corking the flask, the contents are shaken for ten minutes, then 20 c.c. more of ethyl acetate added, and the whole allowed to stand for a quarter of an hour with occasional gentle agitation. The ethyl acetate layer is then first

transferred as completely as possible on to a smooth filter of 8 cm. diameter, 10 c.c. of ethyl acetate added to the aqueous liquid remaining in the flask, the mixture agitated for a moment, and the ethyl acetate layer then again brought on to the filter. After the ethereal liquid has ceased to pass, the aqueous solution is poured on the filter, without regard to the crystals adhering to the sides of the flask, and the filter as well as the flask washed three times with water which has been saturated with ether, using 5 c.c. each time. When the liquid has thoroughly drained from the flask, and ceased to drop from the filter, both the flask and filter are dried at 100°.

In order to determine the amount of morphine gravimetrically, the dried contents of the filter are transferred to the previously tared flask by means of a camel's-hair brush, and the whole heated at 100° until the weight is constant. The weight of substance, when multiplied by 25, then represents the percentage amount of anhydrous morphine in the opium. The German Pharmacopœia directs, however, that the morphine shall ultimately be determined by the following volumetric method :— The crystals of morphine, as obtained above, are dissolved in 25 c.c. of $N/10$ hydrochloric acid, the solution poured into a graduated flask of 100 c.c. capacity, the filter, flask, and stopper then carefully washed with water, and the solution finally diluted to the measure of 100 c.c. 50 c.c. of this solution, representing 2 g. of powdered opium, are placed in a flask of about 200 c.c. capacity, and about 50 c.c. of water added, together with so much ether that the latter forms a layer about 1 cm. in depth. After the addition of 10 drops of iodo-eosine solution, $N/10$ potassium hydroxide is allowed to flow into the liquid, shaking actively after each addition, until the lower aqueous layer has assumed a pale red colour. For this purpose not more than 4·1 c.c. of $N/10$ potassium hydroxide should be required, so that at least 8·4 c.c. of $N/10$ hydrochloric acid are used for the neutralisation of the morphine present. This corresponds to a minimum of 12 per cent. of morphine in the opium, since 1 c.c. $N/10$ hydrochloric acid $= 0·02852$ g. of morphine, $C_{17}H_{19}O_3N$, with iodo-eosine as the indicator.

The British Pharmacopœia (1898) requires that opium dried at 100° should contain about 10 per cent. of anhydrous morphine. The United States Pharmacopœia (eighth revision) specifies that opium in its normal moist condition should contain not less than 9 per cent. of crystallised morphine, $C_{17}H_{19}O_3N$, H_2O, or, when dried at 85° not less than 12 per cent. nor more than 12·5 per cent. of crystallised morphine. It should be noted, however, that these percentages of morphine are based upon the methods of assay prescribed by the respective pharmacopœias, since different methods are likely to yield somewhat divergent results.

(d) *Microscopic Test*, especially for starch.

The following variations in composition have been found in the examination of opium :—

Moisture	. . .	7·35 to 24·13 per cent.
Ash	. . .	3·55 „ 5·49 „
Aqueous extract	.	45·00 „ 45·25 „
Morphine	. .	9·98 „ 15·82 „

VEGETABLE DRUGS.

The method of examination of vegetable drugs should be of an individual character, in accordance with the purpose for which the drug is to be used, and with due consideration of the preparation that is to be made from it. In cases where official preparations are concerned the method of testing adopted should be in accord with the respective directions given in the current pharmacopœias. Since these examinations only involve the determination of comparative values, and not exact figures for the purpose of manufacture, H. Mix and K. Dieterich regard it as sufficient to extract the drug once only, and to allow not more than forty-eight to sixty hours for the operations of expression, filtration, evaporation, and drying to constant weight.

I. BARKS.

Cascara Sagrada.

The dried bark of *Rhamnus Purshiana*, DC.

Determination of Extract.—The bark is extracted by the following methods, according as it is to be used for the preparation of (1) aqueous extract ; (2) alcoholic extract ; or (3) liquid extract.

1. As indicated under Ergot (p. 225).

2. As indicated under Flowers (III.), either with 68 per cent. alcohol, or with a mixture of 2 parts by weight of 90 per cent. alcohol and 3 parts of water.

3. Like the preceding, with a mixture of 1 part by weight of 90 per cent. alcohol and 2 parts of water.

The German Pharmacopœia requires that the bark, when completely extracted with a mixture of 3 parts of alcohol and 7 parts of water, should yield at least 24 per cent. of extract, and that, when incinerated, it should leave not more than 6 per cent. of residue.

Cascarilla.

The dried bark of *Croton Eluteria*, Bennett.

Determination of Extract.—As described in the introduction to Leaves (p. 239), in the proportion of 10 : 200.

Cinchona.

The British, United States, and German Pharmacopœias all recognise the dried bark of the stem and branches of cultivated plants of *Cinchona succirubra*, Pavon. In addition to the latter the United States Pharmacopœia, under the general title of *Cinchona*, comprehends the dried bark of *Cinchona Ledgeriana*, Moens, *C. Calisaya*, Weddell, *C. officinalis*, Linné, and hybrids of these with other species of *Cinchona*.

(a) *Aqueous Extract.*—10 g. of the finely powdered bark are mixed in a beaker with 100 c.c. of cold water, and the mixture allowed to stand for twenty-four hours, with frequent stirring. It is then allowed to settle, 20 c.c. of the filtered liquid (= 2 g. of bark) evaporated, and the residue dried until of constant weight.

(b) *Alcoholic Extract.*—Proceed as under (*a*), but with the use of 68 per cent. alcohol.

The following yields of extract have been obtained :—

Dry aqueous extract	.	.	. 11·1 to 26·0 per cent.
Dry alcoholic extract	.	.	. 34·0 ,, 39·5 ,,

(c) *Determination of Alkaloid.*—The following method is that of the German Pharmacopœia :—

To 12 g. of the finely powdered bark, contained in a flask, are added 30 g. of chloroform and 30 g. of ether (sp. gr. 0·720), and, after vigorous shaking, 5 g. of solution of sodium hydroxide (15 per cent.) and 5 g. of water. The mixture is then allowed to stand for three hours, with frequent vigorous shaking. 60 g. of ether are subsequently added, the whole being well shaken, and, after the liquid has become clear, 80 g. of the chloroform-ether mixture (= 8 g. of cinchona bark) are filtered through a dry, well-covered filter into a flask, and about two-thirds of the solvent distilled off. The cooled residue is transferred to a glass separator (I.), the flask washed three times with a mixture of 2 parts of chloroform and 5 parts of ether, using 5 c.c. each time, then once with 20 c.c. of dilute hydrochloric acid (containing 1 per cent. of acid of sp. gr. 1·126), these liquids being also brought into the separator, and, after the addition of so much ether that the chloroform-ether mixture floats on the surface of the acid liquid, the entire mixture is vigorously shaken for two minutes. When the liquids have become clear, the hydrochloric acid solution is allowed to flow into another separator (II.), and the ethereal liquid shaken twice successively in the same manner with the above-mentioned dilute hydrochloric acid, using 5 c.c. each time.

To the combined hydrochloric acid liquids are added 5 c.c. of chloroform, then a solution of sodium carbonate until the reaction is

alkaline, and the mixture at once shaken vigorously for two minutes. When the liquids have become perfectly clear, the chloroform extract is allowed to flow into another separator (III.), and the alkaline liquid shaken three times successively with chloroform, using 5 c.c. each time. To the combined chloroform extracts are added 25 c.c. of $N/10$ hydrochloric acid, and so much ether that the chloroform-ether mixture floats on the surface of the acid liquid, after which the whole is well shaken for two minutes. When it has become perfectly clear, the acid liquid is filtered through a small filter, moistened with water, into a graduated flask of 100 c.c. capacity, the chloroform-ether mixture shaken three times successively for two minutes with water, using 10 c.c. each time, these aqueous liquids being also passed through the same filter, which is finally washed with water, and the entire aqueous, acid liquid diluted with water to 100 c.c. 50 c.c. of this liquid (=4 g. of cinchona bark) are placed in a flask, about 50 c.c. of water added, and then a freshly prepared solution of a fragment of hæmatoxylin in 1 c.c. of alcohol. Subsequently $N/10$ potassium hydroxide solution is added to the liquid, with gentle agitation, until the mixture assumes a deep yellow colour, which by vigorous agitation quickly passes into bluish-violet. For this purpose not more than 4.1 c.c. of $N/10$ potassium hydroxide solution should be required, so that at least 8.4 c.c. $N/10$ hydrochloric acid would be used up for the neutralisation of the alkaloids present. This would correspond to a minimum of 6.5 per cent. of alkaloids in the bark (1 c.c. $N/10$ hydrochloric acid = 0.0309 g. quinine and cinchonine, using hæmatoxylin as the indicator).

5 c.c. of the alkaloid solution which was not used for the titration, when mixed with 1 c.c. of chlorine water, should give a green coloration on the addition of solution of ammonia.

Standards for Alkaloid.—The German Pharmacopœia requires that red cinchona bark, when assayed by the above method, should yield at least 6.5 per cent. of alkaloids of the composition $C_{20}H_{24}O_2N_2$ (quinine) and $C_{19}H_{22}ON_2$ (cinchonine), having an average molecular weight of 309. The British Pharmacopœia requires between 5 and 6 per cent. of total alkaloids, of which not less than half should consist of quinine and cinchonidine, when estimated by the official method. The United States Pharmacopœia requires for *Cinchona succirubra* not less than 5 per cent. of anhydrous cinchona alkaloids; for the species mentioned under *Cinchona* not less than 5 per cent. of total anhydrous cinchona alkaloids, and at least 4 per cent. of anhydrous ether-soluble alkaloids, when assayed by the official process.

Since the various pharmacopœias prescribe different methods of assay, and the percentage of alkaloids required to be contained in a bark is based on a particular method, it is obvious that this is to be

considered in connection with the valuation of any given species of cinchona which is to be used for pharmacopœial purposes.

Cinnamon and Cassia.

The true Cinnamon consists of the dried inner bark of the shoots of *Cinnamomum zeylanicum*, Breyne, and is distinguished in commerce as Ceylon Cinnamon.

Cassia bark is obtained from one or more undetermined species of *Cinnamomum* grown in China, and is also known as Chinese Cinnamon.

The British and German Pharmacopœias recôgnise only Ceylon Cinnamon, whereas the United States Pharmacopœia also includes Saigon Cinnamon, which is the bark of an undetermined species of *Cinnamomum*.

Determination of Extract.—The yield ôf aqueous extract is determined as stated under Ergot, and that of alcoholic extract by the method described under Flowers (III.), with the use of 68 per cent. alcohol.

Determination of Aldehyde.—The yield of cinnamic aldehyde may be determined by the method of J. Hanus.[1]

The German Pharmacopœia requires that cinnamon bark should yield on ignition not more than 5 per cent. of ash.

Condurango.

The probable botanical source of this bark is *Marsdenia cundurango*, Reichenbach fils.

Determination of Extract.—When the bark is to be used for the preparation of extract, the yield of alcoholic extract is determined as under Flowers (III.), with the use of a mixture of 2 parts by weight of 90 per cent. alcohol and 1 part of water. For the preparation of a liquid extract it is treated in the same manner, but with a mixture of 1 part by weight of alcohol and 3 parts of water. For a tincture the extraction is conducted with 68 per cent. alcohol.

Frangula.

The dried bark of *Rhamnus frangula*, Linné.

Determination of Extract.—The bark is extracted by one of the following methods, according to its intended use for the preparation of (1) an aqueous extract; (2) an alcoholic extract; (3) a liquid extract; or (4) a tincture.

(1) It is extracted with cold water in the manner described under Ergot (p. 225), or with boiling water as described in the introduction to Leaves (p. 239), in the proportion of 10 : 200.

[1] *Z. Unters. Nahr. u. Genussm.*, 1903, **6**, 817 ; *J. Soc. Chem. Ind.*, 1903, **22**, 1154.

(2) In the manner described under Flowers (III.), with a mixture of 2 parts by weight of 90 per cent. alcohol and 3 parts of water.

(3) In the same manner, with a mixture of 3 parts by weight of 90 per cent. alcohol and 7 parts of water.

(4) In the same manner, but with 68 per cent. alcohol.

II. BULBS.

Squill.

Squill consists of the bulb of *Urginea maritima* (Linné), Baker, divested of its dry, membranous outer scales, cut into slices, and dried.

Determination of Extract.—The squill, in moderately fine powder, is extracted with either cold or hot water, or with 68 or 90 per cent. alcohol, according to the methods which have been described, and adhering as closely as possible to the directions for making the respective preparations.

The German Pharmacopœia requires that squill shall yield on ignition not more than 5 per cent. of ash.

III. FLOWERS.

In the case of flowers the alcoholic extract is generally determined in accordance with the following method :—

(a) *Alcoholic Extract.*—To 10 g. of the ground flowers, contained in a flask, are added 100 c.c. of a mixture of 1 part by weight of alcohol and 2 parts of water. The flask is then closed, allowed to stand for twenty-four hours, with frequent shaking, and, after the material has deposited, the liquid is filtered. 20 c.c. of the filtrate (= 2 g. of the drug) are then evaporated in a tared dish, and the residue dried at 100° until the weight is constant.

(b) The official flowers should conform to the requirements of the respective pharmacopœias.

Chamomile Flowers.

The Chamomile Flowers of the British and United States Pharmacopœias consist of the dried flower heads of *Anthemis nobilis*, Linné, whereas the German Pharmacopœia recognises only the dried flower heads of *Matricaria chamomilla*, Linné, which are commonly known as German Chamomile.

Determination of Extract.—The German chamomile flowers, according to their intended use for the preparation of (1) tincture ; (2) extract or syrup ; or (3) oil, are extracted by one of the following methods :—

(1) As described above, with 68 per cent. alcohol.

(2) As described above, with a mixture of 2 parts by weight of 90 per cent. alcohol and 3 parts of water.

(3) In the same manner, with 200 c.c. of a mixture of 150 g. of 90 per cent. alcohol and 2 g. of a solution of ammonia (sp. gr. 0·960).

All extractions of chamomile flowers should be conducted in the proportion of 10 g. of the flowers to 200 c.c. of the respective liquid.

Red Poppy Petals.

Red Poppy petals are obtained from *Papaver Rhoeas*, Linné.

Determination of Extract.—This is conducted according to the method described in the introduction to Leaves (p. 239), in the proportion of 10 : 200, but the temperature of extraction should not exceed about 35°-40°, and 0·2 g. of citric acid should be added to 10 g. of the red poppy petals or to 200 c.c. of water respectively.

Rose Petals.

This title refers to the petals of the Pale Rose or Cabbage Rose, which are obtained from *Rosa centifolia*, Linné.

Determination of Extract.—The extraction is conducted in the proportion of 10 parts of the petals to 200 parts of liquid by one of the following methods, according to the use of the petals for the preparation of (1) an alcoholic extract ; or (2) for honey of rose.

(1) By the above general method, with the use of 68 per cent. alcohol.

(2) As described in the introduction to Leaves (p. 239), in the proportion of 10 : 200.

IV. FRUITS.

Buckthorn Berries.

The fruit of *Rhamnus cathartica*, Linné.

Determination of Extract.—The well-crushed berries are extracted by the use of 10 parts of berries to 100 parts of solvent, as described in the introduction to Leaves (p. 239).

Capsicum. Spanish Pepper. Cayenne Pepper.

In the German Pharmacopœia Capsicum is defined as the dried, ripe fruit of *Capsicum annuum*, Linné, whereas the British and United States Pharmacopœias recognise the smaller fruit of *Capsicum minimum*, Roxb. (*C. fastigiatum*, Blume).

Determination of Extract.—According to the intended use of capsicum for the preparation of (1) a liquid extract; (2) a tincture; or (3) a thick extract, it is extracted with one of the following solvents, as indicated under Flowers (III.).

(1) With 90 per cent. alcohol.

(2) With 68 per cent. alcohol.

(3) With a mixture of 2 parts by weight of alcohol and 3 parts of water.

The German Pharmacopœia requires that powdered capsicum should yield on ignition not more than 6·5 per cent. of ash.

Elder Berries.

The fruit of *Sambucus nigra*, Linné.

Determination of Extract.—This is conducted as indicated under Buckthorn berries.

Fennel.

The ripe fruit of *Fœniculum capillaceum*, Gilibert.

Determination of the Essential Oil (according to K. Dieterich).—10 g. of the finely crushed fruit are distilled in a current of steam until the distillate (about 500 c.c.) no longer possesses an odour. The distillate is then saturated with common salt and allowed to stand for twenty-four hours, after which the oil is extracted with 50 c.c. of ether by shaking in a separator. The ethereal liquid is filtered through a little well-dried salt, the latter subsequently washed with 20 c.c. of ether, and the combined liquids allowed to evaporate spontaneously in a beaker which is covered with finely perforated filter paper. When the ether has completely evaporated, the residue is dried for twelve hours in a desiccator, and weighed.

The yield of essential oil has been found to be from 3·0 to 4·0 per cent.

The German Pharmacopœia requires that powdered fennel fruit should yield on ignition not more than 10 per cent. of ash.

Juniper Berries.

The dried, ripe fruit of *Juniperus communis*, Linné.

Determination of Extract.—As described in the introduction to Leaves (p. 239).

The juniper berries are previously well crushed, but extracted only in the proportion of 10 parts of berries to 100 parts of liquid, and the heating for a quarter of an hour in a hot-water bath is omitted.

The German Pharmacopœia requires that powdered juniper berries should yield on ignition not more than 5 per cent. of ash.

Parsley Fruit.

The fruit of *Carum Petroselinum*, Benth. et Hook.

Determination of the Essential Oil (according to K. Dieterich).—As described under Fennel, and according to the Supplement to the German Pharmacopœia, 4th edition.

Poppy Capsules.

Poppy capsules or heads are the dried, immature fruits of *Papaver somniferum*, Linné.

Determination of Extract.—This is conducted as described under Flowers (III.), with 100 c.c. of a mixture of 1 part by weight of 90 per cent. alcohol and 9 parts of water.

V. HERBS.

The general directions for the examination of herbs consist in determining either the yield of alcoholic extract, as described under Flowers (III.), or the aqueous extract, as described under Leaves (VI.).

When the herbs are to be used for making extracts, the prescribed directions for the respective extract should be strictly followed. The herbs should be used in a finely cut state.

Carduus Benedictus (Blessed Thistle).

The dried leaves and flowering branches of *Cnicus benedictus*, Linné.

Determination of Extract.—As described under Alexandrian Senna leaves (p. 244).

Linaria (Common Toad-flax).

The flowering plant of *Linaria vulgaris*, Miller.

Determination of Extract.—As described under Flowers (III.), with the use of 100 c.c. of a mixture of 150 g. of 90 per cent. alcohol and 5 g. of a solution of ammonia (sp. gr. 0·960).

Marjoram (Sweet Marjoram).

The leaves and flowering stems of *Origanum Majorana*, Linné.

Determination of Extract.—As described under Linaria.

Milfoil or Yarrow.

The flowering plant of *Achillea Millefolium*, Linné.

Determination of Extract.—As described under Flowers (III.), with a mixture of 2 parts by weight of 90 per cent. alcohol and 3 parts of water, and in the proportion of 10 g. of herb to 200 c.c. of liquid.

VI. LEAVES.

The general method for the examination of leaves consists in determining the yield of water-soluble extract. The procedure is as follows :—

(a) *Determination of Extract.*—To 10 g. of the finely cut leaves, contained in a tared beaker, 100 g. of boiling water are added, the

whole heated for ten to fifteen minutes in a hot-water bath, and allowed to stand for twenty-four hours. The amount of evaporated water is then replaced, the liquid filtered, 20 c.c. of the filtrate (= 2 g. of the drug) evaporated to dryness, and the residue heated at 100° until of constant weight.

(b) Those leaves which are officially recognised are also to be tested according to the respective pharmacopœia.

The examination is somewhat differently conducted with belladonna, coca, digitalis, senna, and menyanthes leaves.

Belladonna (Deadly Nightshade).

The dried leaves of *Atropa Belladonna*, Linné, which, according to the German Pharmacopœia, should be collected from plants growing wild and at the time of flowering.

Determination of Hyoscyamine, $C_{17}H_{23}O_3N$.—The following method is that of the German Pharmacopœia :—

To 20 g. of finely powdered belladonna leaves, contained in a flask, are added 120 g. of ether, and, after vigorous shaking, 5 g. of a solution of sodium hydroxide (15 per cent.) and 5 g. of water. The mixture is then allowed to stand for an hour, with frequent and vigorous shaking. When the liquid has become perfectly clear, 60 g. of the ethereal solution (= 10 g. of belladonna leaves) are filtered through a dry, well-covered filter into a flask, and about two-thirds of the ether distilled off. The cooled residue is transferred to a glass separator (I.), the flask washed three times with ether, using 5 c.c. each time, and then once with 10 c.c. of dilute hydrochloric acid (1 part of acid, sp. gr. 1·126, to 49 parts of water), these liquids being also brought into the separator, and the whole shaken vigorously for two minutes. When the liquids have become perfectly clear, the hydrochloric acid solution is run into another separator (II.), and the ethereal liquid again shaken in the same manner with two successive portions, of 5 c.c. each, of dilute hydrochloric acid (1:49), the latter having previously been used for the further rinsing of the flask.

To the combined hydrochloric acid extracts are added 5 c.c. of chloroform, then sufficient solution of sodium carbonate to impart an alkaline reaction, and the mixture at once shaken vigorously for two minutes. After having become perfectly clear, the chloroform extract is run into another separator (III.), and the aqueous, alkaline liquid again shaken three times successively with chloroform, using 5 c.c. each time. To the combined chloroform extracts 20 c.c. of $N/10$ hydrochloric acid are then added, and so much ether that the chloroform-ether mixture floats on the surface of the hydrochloric acid, after which the whole is shaken vigorously for two minutes. After having become perfectly clear, the acid liquid is filtered through a small

filter, previously moistened with water, into a colourless glass flask of about 200 c.c. capacity, the chloroform-ether mixture again shaken three times successively for two minutes with water, using 10 c.c. each time, these liquids being passed through the same filter, which is subsequently washed with water, and the entire liquid finally diluted to about 100 c.c.

After having added so much ether that the layer of the latter is about 1 cm. in depth, and 10 drops of iodo-eosine solution, $N/100$ solution of potassium hydroxide is added to the liquid, the mixture being actively shaken after each addition, until the lower aqueous layer has assumed a pale red colour. For this purpose not more than 9·6 c.c. of $N/100$ potassium hydroxide should be required, so that at least 10·4 c.c. of $N/100$ hydrochloric acid would be used up for the neutralisation of the alkaloid present. This would correspond to a minimum of 0·3 per cent. of hyoscyamine in the leaves (1 c.c. $N/100$ hydrochloric acid = 0·00289 g. hyoscyamine, using iodo-eosine as the indicator).

The United States Pharmacopœia, in conformity with the above standards, requires that belladonna leaves should yield not less than 0·3 per cent. of mydriatic alkaloids, when assayed by the official process.

The amount of dry, aqueous extract yielded by belladonna leaves has been found to vary from 23·9 to 32·9 per cent.

The German Pharmacopœia requires that powdered belladonna leaves should yield on ignition not more than 15 per cent. of ash.

Coca.

The dried leaves of *Erythroxylum Coca*, Lamarck.

Determination of Cocaine (according to C. C. Keller).—To 12 g. of powdered coca leaves, contained in a flask of 150 c.c. capacity, are added 120 g. of ether, then after fifteen minutes 10 c.c. of a solution of ammonia (sp. gr. 0·960), and the whole frequently and vigorously shaken. After half an hour, 20 c.c. of water are added, and the separation of the drug effected by prolonged, vigorous shaking. Subsequently 100 g. of the dark green, ethereal solution (= 10 g. of the leaves) are decanted, and allowed to stand for a short time, when a small amount of the finest particles of the drug, together with drops of water, will be deposited at the bottom of the flask. The clear solution is then transferred to a separator, shaken first with 50 c.c. of 0·5 per cent. hydrochloric acid, and then once again with 25 c.c. of the same dilute acid. The acid, aqueous liquid is placed in another separator, made alkaline with ammonia, and shaken twice successively with ether, using 40 c.c. each time. The clear, ethereal solution is then transferred to a tared flask, the ether distilled off, and the residue dried in a water-bath and weighed.

III   Q

The standard is about 1 per cent. of cocaine.

Although the German Pharmacopœia restricts the definition of Coca to the leaves of *Erythroxylum Coca*, which is the Bolivian or Huanuco variety, the British and United States Pharmacopœias also recognise the Peruvian or Truxillo Coca, from *E. Truxillense*, Rusby. The latter requires the dried leaves of either species to contain not less than 0·5 per cent. of the ether-soluble alkaloids of Coca, when assayed by the prescribed method.[1]

Digitalis.

The dried leaves of flowering plants of *Digitalis purpurea*, Linné.

Determination of Digitoxin (according to C. C. Keller).—20 g. of the leaves are thoroughly extracted in a suitable apparatus, or by percolation, with 70 per cent. alcohol. The completeness of this operation may be controlled by allowing 3-4 c.c. of the last portions of the percolate to evaporate, taking up the residue with about 3 c.c. of water and two drops of hydrochloric acid, and testing the filtered liquid with a solution of tannin, when no appreciable turbidity should ensue.

The entire percolate is evaporated in a porcelain dish on the water-bath, with active stirring, to about 25 g., in order to remove the alcohol, the residue then taken up with water, washed into a flask of 250 c.c. capacity, and the total weight brought to 222 g. To this turbid solution of the extract are added 25 g. of a solution of basic acetate of lead, when a copious precipitate will be formed. By a gentle swaying of the flask a uniform mixture is obtained, but it should not be strongly shaken, otherwise much froth will be produced, which renders the subsequent filtration more difficult. The very voluminous precipitate, when washed and dried, weighs about 7 g., so that 12 g. of the liquid correspond to 1 g. of digitalis leaves. The thick mixture is brought on to a filter of about 18 cm. diameter, 132 g. of the filtrate collected, and to this clear, pale yellow liquid a solution of 5 g. of sodium sulphate in 7 g. of water is added, to precipitate the excess of lead. If the precipitation is conducted in an Erlenmeyer flask, which after some time is placed in a sharply inclined position, the lead sulphate will be deposited in such a manner that in the course of four or five hours 130 g. of the liquid (= 10 g. of digitalis leaves) can be decanted perfectly clear, and the difficulty of collecting and washing the precipitate on a filter is thus avoided. The liquid is then placed in a separator, and 2 c.c. of a solution of ammonia (10 per cent.) added, when it will become somewhat darker in colour, but must remain perfectly clear, indicating that only traces of lead remain; otherwise an emulsion will be formed by the subsequent extraction. It is then

[1] For a comprehensive review of the methods of assay suggested for coca leaves, see *Arch. Pharm.*, 1910, **248**, 303-336 ; *J. Soc. Chem. Ind.*, 1910, **29**, 897.

shaken four or five times successively with chloroform, using 30 c.c. each time. The united and only slightly turbid chloroform solutions are passed through a double, pleated filter of 8-9 cm. diameter, which has previously been moistened with chloroform, when the liquid will be obtained perfectly clear. It is then transferred to a tared Erlenmeyer flask, and the chloroform distilled off in a water-bath, when the digitoxin will remain as a yellow varnish. If the digitoxin is extracted from an acid instead of from an alkaline solution, it will be obtained in a much less pure form.   •

The crude digitoxin contains small amounts of fat, and especially the odorous principles of the digitalis, and therefore requires purification. For this purpose the residue is dissolved in 3 g. of chloroform, and to the solution are added 7 g. of ether and 50 g. of light petroleum, when the digitoxin will be precipitated in white flakes, which are rapidly deposited, while the liquid, if actively shaken, will become perfectly clear. In order to obtain the precipitate in a suitable condition for weighing, a variety of methods may be adopted.

The precipitate may be collected on a small, pleated filter, and the flask and filter washed with a little light petroleum, the small funnel being meanwhile kept covered with a watch-glass. After the light petroleum has passed through, the funnel is again placed in the neck of the flask, to the sides of which a portion of the digitoxin will have adhered, and the contents of the filter, while still moist, again brought into solution by pouring some hot absolute alcohol upon it. The alcoholic solution is evaporated, about 5 c.c. of ether added to the residue, and the ether then removed by heating in a water-bath, when the varnish-like digitoxin will be partially changed into the crystalline form. The residue is finally dried in·a water-bath and weighed.

Another method is as follows :—The flask with the precipitated digitoxin is placed in a sharply inclined position, and allowed to remain undisturbed for some hours, until the flakes have been well deposited, when the light petroleum is decanted, so far as this may be possible without loss. The remaining contents of the flask are weighed, and these evaporated at a gentle heat, which is best effected by blowing a warm current of air, by means of a hand-bellows, into the flask. Care should be taken not to place the flask in a hot-water bath, otherwise the contents will be thrown out with explosive violence. The digitoxin will remain as a white powder, which can now be weighed, but a correction of the weight is necessary. If it be assumed that the crude digitoxin weighed 0·062 g., the purified substance 0·048 g., the decanted light petroleum 50 g., and the contents of the flask which were evaporated 10 g., the latter would still have contained 0·0028 g. of impurities. The purified digitoxin would therefore be calculated as 0·048 − 0·0028 = 0·0452 g. or 0·452 per cent.

Determination of Extract.—The yield of aqueous extract is determined by the cold process, as described under Ergot (p. 225).

The following values have been obtained :—

Digitoxin	0·26 to 0·62 per cent.
Dry, aqueous extract, up to . .	36 per cent.

Menyanthes (Buckbean, Bogbean, Marsh Trefoil).

The leaves of *Menyanthes trifoliata*, Linné.

Determination of Extract.—As described in the introduction to Leaves (p. 239), in the proportion of 10 to 200.

Senna (Alexandrian).

The dried leaflets of *Cassia acutifolia*, Delile.

Determination of Extract.—In the same manner as with Menyanthes.

The German Pharmacopœia recognises only the Indian or Tinnevelly Senna, which consists of the dried leaflets of *Cassia angustifolia*, Vahl, and requires that the powdered leaves should yield on ignition not more than 12 per cent. of ash.

Strammonium.

The leaves of *Datura Strammonium*, Linné, collected at the time of flowering.

Determination of Extract.—This is conducted as follows, according to the use of the leaves for the preparation of (1) tincture ; (2) oil ; or (3) extract.

(1) By extraction with pure alcohol, as described in the introduction to Flowers (III.) (p. 236).

(2) By extraction with a mixture of 150 g. of 90 per cent. alcohol and 4 g. of a solution of ammonia (sp. gr. 0·960), in the same manner as the preceding.

(3) By extraction with either cold or hot water. 10 g. of the sample are extracted with 100 g. of water ; the extraction with hot water is carried on for a quarter of an hour in a hot-water bath, the water lost by evaporation being made good.

The United States Pharmacopœia directs the assay of strammonium leaves for alkaloid to be conducted in the same manner as prescribed for belladonna leaves, and requires that they shall contain not less than 0·25 per cent. of mydriatic alkaloids.

The German Pharmacopœia requires that powdered strammonium leaves should yield on ignition not more than 20 per cent. of ash.

Uva Ursi.

The dried leaves of *Arctostaphylos Uva-Ursi* (Linné), Sprengel.

Determination of Extract.—By extraction with cold water, as indicated under Ergot (p. 225).

By extraction with hot water, as described in the introduction to Leaves (p. 239), in the proportion of 10 : 200.

By extraction with a mixture of equal parts by weight of 90 per cent. alcohol and water, as described in the introduction to Flowers (III.) (p. 236).

VII. RHIZOMES.

The rhizomes are examined in precisely the same manner as the roots, for which the details are given below (p. 247). The yield of either aqueous or alcoholic extract is determined as the directions for making the extract may require. The tests of the Pharmacopœia are also to be considered. In the case of calamus rhizome the yield of alcoholic extract is determined.

Galangal.

The dried rhizome of *Alpinia officinarum*, Hance.

Determination of Extract.—By extraction with 68 per cent. alcohol in the usual manner.

Ginger.

The dried rhizome of *Zingiber officinale*, Roscoe.

Determination of Extract.—This is conducted either by extracting with a mixture of 1 part of 90 per cent. alcohol and 8 parts of water, or with 68 or 90 per cent. alcohol.

The German Pharmacopœia requires that powdered ginger should yield on ignition not more than 7 per cent. of ash.

Hydrastis (Golden Seal).

The dried rhizome and roots of *Hydrastis canadensis*, Linné.

(a) *Determination of Alcoholic Extract.*—This is conducted according to the general method described under Roots (VIII.). The yield should be not less than 20 per cent. It has been found to vary from 20·04 to 28·0 per cent.

(b) *Determination of Hydrastine.*—The following method is that of the German Pharmacopœia:—To 6 g. of hydrastis rhizome in moderately fine powder, contained in a flask, are added 60 g. of ether, and, after vigorous shaking, 10 c.c. of a solution of ammonia (sp. gr. 0·960), the mixture being then allowed to stand for three hours, with frequent and vigorous shaking. When the liquid has become perfectly clear, 40 g. of the ethereal solution (= 4 g. of hydrastis rhizome) are filtered through a dry, well-covered filter into a flask, and the ether distilled off. The residue is then gently heated with 10 c.c. of dilute hydrochloric acid (1 part of acid, sp. gr. 1·126, to 99 parts of

water), and the solution passed through a small filter, previously moistened with water, into a separator, the flask being washed twice successively with dilute hydrochloric acid of the above strength, using 5 c.c. each time. These liquids are passed through the same filter into the separator, the filter being finally washed with a little water. To the united acid liquids are added 40 c.c. of ether, the mixture being vigorously shaken, and then sufficient solution of ammonia to impart an alkaline reaction, after which the mixture is at once shaken vigorously for two minutes. When it has become perfectly clear, the aqueous liquid is drawn off, the ethereal liquid remaining in the separator again shaken, and, when clear, 30 c.c. of it (= 3 g. of hydrastis rhizome) are transferred to a light, tared flask. The ether is then allowed to evaporate at a moderate heat, and the residue dried at 100° until the weight remains constant. The amount of residue should be not less than 0.075 g., corresponding to at least 2.5 per cent. of hydrastine, $C_{21}H_{21}O_6N$.

The same percentage of hydrastine is required by the United States Pharmacopœia, when determined by the prescribed method of assay.

Male Fern.

The rhizome of *Aspidium Filix-mas* (Linné), Swartz, collected in the autumn, divested of the roots, leaves, and dead portions, and carefully dried.

The United States Pharmacopœia, under the title of *Aspidium*, recognises the dried rhizome of *Dryopteris Filix-mas* (Linné), Schott, or of *D. marginalis* (Linné), Asa Gray.

Determination of Extract.—10-20 g. of the rhizome, dried and in moderately fine powder, are extracted in a Soxhlet apparatus for one and a half to two hours with ether (sp. gr. 0.720). The ether is then evaporated off in a tared flask, and the residue dried and weighed.

Rhubarb.

The dried rhizome of *Rheum palmatum*, Linné, and *R. officinale*, Baillon.

Determination of Extract.—Either the yield of aqueous extract is determined by the cold process, as described under Roots (VIII.), or the extraction may be conducted with dilute alcohol according to the following method of the German Pharmacopœia :—

To 5 g. of rhubarb, in fine powder, are added 50 c.c. of a mixture of equal parts by weight of 90 per cent. alcohol and water, and the mixture allowed to stand for twenty-four hours, with frequent agitation ; 20 c.c. of the clear, filtered liquid are then evaporated in a tared dish, and the residue dried at 105° until the weight is constant. The weight

should be not less than 0·7 g., corresponding to at least 35 per cent. of extract.

The powdered rhubarb should yield on ignition not more than 12 per cent. of ash.

VIII. ROOTS.

The directions, in general, are as follows, according to whether the yield of aqueous or alcoholic extract is to be determined:—

(a) *Aqueous Extract.*—To 10 g. of the finely powdered root are added 100 g. of cold water, and the mixture allowed to stand for twenty-four hours, with frequent stirring; the liquid is then passed through a dry filter, 20 c.c. of the filtrate (= 2 g. of the root) evaporated in a tared dish, and the residue dried at 100° until of constant weight.

(b) *Alcoholic Extract.*—The procedure is the same as in the case of the aqueous extract, but with the use of a mixture of equal parts of alcohol and water.

Belladonna.

The dried root of *Atropa Belladonna*, Linné.

Determination of Alkaloid (according to C. C. Keller).—To 25 g. of dried belladonna root, in the form of powder, and contained in a flask, are added 90 g. of ether and 30 g. of chloroform, and the mixture allowed to stand for ten minutes, with frequent shaking. 10 g. of a solution of ammonia (sp. gr. 0·960) are then added, and the maceration continued for half an hour, the mixture being repeatedly shaken. Subsequently 15 g. of water are added, the whole shaken vigorously for a few minutes, or until the powdered drug has agglomerated, and 100 g. of the clear liquid then decanted. This is shaken three times successively with 1 per cent. hydrochloric acid, the combined acid liquids made alkaline with ammonia, these extracted with a mixture of chloroform and ether, the ethereal liquid evaporated in a tared flask, and the residue weighed. The latter is subsequently dissolved in a little alcohol, the solution diluted with water, and titrated with $N/10$ hydrochloric or sulphuric acid with the use of hæmatoxylin as the indicator. 1 c.c. of $N/10$ acid=0·0289 g. of atropine.

The yield of alkaloid should be not less than 0·5 per cent. (*cf.* also the method of assay described under belladonna leaves, Section VI., p. 240).

The following variations in yield have been found:—

Aqueous extract .   .   . 20·0 to 23·33 per cent.
Alkaloid .   .   .   . 0·63 „ 0·70 „

The United States Pharmacopœia requires that belladonna root should yield not less than 0·45 per cent. of mydriatic alkaloids, when assayed by the method prescribed for belladonna leaves.

Gentian.

The dried rhizome and roots of *Gentiana lutea*, Linné, or of other species of *Gentiana*, of which the German Pharmacopœia specifies *G. pannonica*, Scopoli; *G. purpurea*, Linné; and *G. punctata*, Linné.

Determination of Extract.—For the preparation of extract the root is treated as described for Frangula bark, under (I.) (p. 235); for a liquid extract it is extracted with a mixture of equal parts of alcohol and water; and for a tincture with 68 per cent. alcohol.

Ipecacuanha.

The dried root of *Uragoga ipecacuanha* (Willdenow), Baillon.

(a) *Determination of Extract.*—For the preparation of a liquid extract the root is extracted with 90 per cent. alcohol, for a tincture with 68 per cent. alcohol, and for the preparation of the syrup with a mixture of 1 part of alcohol and 8 parts of water.

(b) *Determination of Alkaloid.*—The following method is that of the German Pharmacopœia. To 12 g. of finely powdered ipecacuanha, contained in a flask, are added 90 g. of ether and 30 g. of chloroform, and, after vigorous shaking, 5 g. of a solution of sodium carbonate (1 : 2) and 5 g. of water, the mixture being then allowed to stand for three hours, with frequent vigorous shaking. When it has become perfectly clear, 60 g. of the chloroform-ether mixture (=6 g. of ipecacuanha) are passed through a dry, well-covered filter into a flask, and the liquid distilled off. The residue is heated with 10 c.c. of dilute hydrochloric acid (1 part of acid, sp. gr. 1·126, to 99 parts of water), the solution passed through a small filter, previously moistened with water, into a separator (I.), the extraction of the residue being then repeated with two successive portions of the same dilute acid as above, using 5 c.c. each time, these liquids passed through the same filter, and the flask and filter finally washed well with water. To the united acid liquids are added 5 c.c. of chloroform, then a solution of sodium carbonate until the reaction is alkaline, and the mixture at once shaken vigorously for two minutes. When perfectly clear, the chloroform solution is run into another separator (II.), and the extraction repeated three times in the same manner with chloroform, using 5 c.c. each time. To the united chloroform solutions are added 10 c.c. of $N/10$ hydrochloric acid, and so much ether that the chloroform-ether mixture floats on the surface of the acid liquid, after which the whole is vigorously shaken for two minutes. When perfectly clear, the acid liquid is passed through a small filter, previously moistened with water, into a flask of 100 c.c. capacity, the chloroform-ether mixture then shaken three times successively for two minutes with water, using 10 c.c. each time, these liquids also passed through the same filter,

which is finally washed with water, and the entire liquid diluted with water to 100 c.c. 50 c.c. of this solution (= 3 g. of ipecacuanha) are transferred to a flask, about 50 c.c. of water added, together with a freshly prepared solution of a fragment of hæmatoxylin in 1 c.c. of alcohol, and so much $N/10$ potassium hydroxide solution run into the liquid, with agitation, that the mixture assumes a deep yellow colour, which, by vigorous agitation, quickly passes into bluish-violet. For this purpose not more than 2·6 c.c. of $N/10$ potassium hydroxide solution should be required, so that at least 2·4 c.c. of $N/10$ hydrochloric acid are used up for neutralising the alkaloids present. This would correspond to a minimum of 1·99 per cent. of alkaloids (1 c.c. $N/10$ hydrochloric acid = 0·02482 g. of alkaloids, calculated as emetine, $C_{30}H_{44}O_4N_2$, with hæmatoxylin as the indicator).

The amount of alkaloid has been found to vary from 0·97 to 3·20 per cent.

The United States Pharmacopœia requires that ipecacuanha shall yield not less than 1·75 per cent. of alkaloids, when assayed according to the prescribed method.

Liquorice (Russian).

The dried root of *Glycyrrhiza glandulifera*, Waldstein and Kitaibel.

Determination of Extract.—If the liquorice is to be used for the preparation of an extract or syrup, the yield of extract is determined by the aid of heat in the following manner:—

To 10 g. of finely cut or coarsely powdered liquorice root, contained in an enamelled vessel which is best weighed with a stirring rod, are added 300 g. of cold water, and the whole allowed to stand for an hour at the ordinary temperature, with frequent stirring. It is then slowly heated to boiling, with frequent stirring, and evaporated to about 210 g. After standing overnight, the evaporated water is replaced, the mixture again stirred vigorously, and the whole brought upon a dry filter; 20 c.c. of the clear filtrate (= 1 g. of root) are then evaporated in a tared porcelain dish and the residue dried until of constant weight.

The yield of extract by the cold process can be determined by extracting with a mixture of 99 g. of cold water and 1 g. of a solution of ammonia (sp. gr. 0·960) in a closed vessel. For the purpose of preparing an alcoholic extract or syrup, the root is extracted with 100 c.c. of a mixture of 49 g. of 90 per cent. alcohol, 48 g. of water, and 3 g. of solution of ammonia (sp. gr. 0·960).

Rhatany.

The dried root of *Krameria triandra*, Ruiz and Pavon (Peruvian Rhatany), and of *K. argentea*, Martius (Para or Brazilian Rhatany).

In addition to these two sorts the United States Pharmacopœia also recognises Savanilla Rhatany, from *K. Ixina*, Linné.

Determination of Extract.—The yield of aqueous extract is determined by the cold process, as described under Ergot (p. 225).

Senega.

The dried rhizome and roots of *Polygala Senega*, Linné.

Determination of Extract.—This is conducted as follows, according to the use of the roots for the preparation of (1) syrup; (2) solid extract; (3) liquid extract; or (4) permanent extract (" Dauerextrakt," Dieterich).

(1) By extraction with a mixture of 1 part of 90 per cent. alcohol and 3 parts of water.

(2) By extraction with a mixture of 2 parts of 90 per cent. alcohol and 3 parts of water.

(3) By extraction with a mixture of 2 parts of 90 per cent. alcohol and 1 part of water.

(4) By extraction with either cold or hot water. The extraction with hot water is carried on for a quarter of an hour in a hot-water bath.

Valerian.

The dried rhizome and roots of *Valeriana officinalis*, Linné.

Determination of Extract.—This is conducted in the usual manner with a mixture of equal parts of alcohol and water.

IX. SEEDS.

Kola Seeds. Kola Nuts.

The seeds of *Cola vera*, Schumann, or of *Cola acuminata*, Schott and Endlicher.

The following methods of examination have been given by K. Dieterich:—

(a) *Determination of Total Alkaloid.*—10 g. of the finely rasped drug, which has been uniformly moistened with water, are mixed with 10 g. of granular, unslaked lime, and the mixture placed in an extraction thimble. This is then extracted with chloroform in a Soxhlet apparatus for three-quarters of an hour, or only so long as the chloroform runs off clear, then washed with chloroform, and the solution evaporated in a dish to approximate dryness. The residue thus obtained is taken up with 20 c.c. of $N/1$ hydrochloric acid, by the aid of a very gentle heat, and the solution filtered into a separator of 100 c.c. capacity, the dish and filter being carefully washed, and the washings added to the acid liquid. The contents of the separator are made strongly alkaline with ammonia, allowed to stand for a quarter of an hour, with frequent shaking, and then extracted with three successive portions of chloroform, using 20 c.c. each time. The united chloroform solutions are finally

evaporated in an Erlenmeyer flask or in a crystallising basin, in the latter case placing the basin in a dish of hot water but not in a steam-bath, in order to prevent loss by the creeping of the liquid, and the caffeine, which is now quite white, dried until the weight is constant. The weight obtained, multiplied by 10, gives the percentage of total alkaloid.

(b) *Free and combined Alkaloid and Fat.*—10 g. of the finely rasped, dry drug are mixed, without previously being moistened, with 10 g. of coarse, purified sand, and extracted for two hours in a Soxhlet apparatus with chloroform. The resulting solution is evaporated, the residue dried until of constant weight, and the total weight of fat and free caffeine determined. This mixture is extracted with boiling water, the solution filtered, and the filter carefully washed. The aqueous solution is evaporated, and the crude caffeine, for the purpose of its purification, taken up with 20 c.c. of $N/1$ hydrochloric acid, as in the determination of total alkaloid. The acid solution is filtered, made alkaline with ammonia, and, after standing for a quarter of an hour, extracted three times successively with chloroform. The united chloroform liquids are then evaporated, and the residue dried until the weight is constant. This weight, multiplied by 10, gives the percentage of free caffeine. By subtracting the amount of the latter from that of the caffeine and fat, as determined above, the amount of fat present is ascertained. The difference between the amount of free caffeine and that of the total alkaloid represents the combined caffeine.

(c) *Determination of Moisture.*—5 g. of the finely rasped drug are dried in a platinum dish at 100° until the weight is constant.

(d) *Determination of Ash.*—The 5 g. of drug which had been used for the determination of moisture are ignited until, after cooling in a desiccator, the weight remains constant.

(e) *Test for Identity.*—20 g. of the drug are mixed with 10 g. of calcined magnesia, the mixture moistened with dilute alcohol, and then extracted with 100 g. of the latter by digestion at a gentle heat, which is best effected by allowing the mixture to stand in a warm room for twelve hours. The liquid is then expressed, filtered, and the filtrate transferred to a white glass vessel, the width of which is at least 10 cm. In a layer of this depth the liquid will show a bluish-green fluorescence, resembling that of curcuma tincture. This reaction is only given by unroasted kola powder.

The following are the minimum and maximum values obtained :—

Total Alkaloid	.	.	.	1·0	to	2·0	per cent.
Free Alkaloid .	.	.	.	0·106	„	0·778	„
Combined Alkaloid	.	.	.	0·788	„	1·282	„
Fat	.	.	.	.	0·324	„	1·298	„
Moisture	.	.	.	9·49	„	13·57	„
Ash	.	.	.	.	2·79	„	5·46	„

Requirements.—The extreme limits should be within the above figures, and the drug should contain the largest possible amount of alkaloid, but not less than 1 per cent., with a preponderating amount of combined alkaloid.

It may be noted that, according to Gadamer, the caffeine is present in only a very loose form of combination, and that, both in the free and combined form, it is probably first produced in the process of drying. The much shorter method of examination of C. C. Keller or that of Siedler,[1] with the use of ammoniacal chloroform, does not give so pure a caffeine, but suffices for a crude analysis.

Black Mustard Seed.

The ripe seed of *Brassica nigra* (Linné), Koch.

Determination of the Essential Oil.—The following method is that of the German Pharmacopœia :—To 5 g. of powdered mustard seed, contained in a flask, are added 100 c.c. of water at 20°-25°. The corked flask is then allowed to stand for two hours, with repeated agitation, 20 c.c. of alcohol and 2 c.c. of olive oil are added, and the mixture distilled with careful condensation. The first 40-50 c.c. which pass over are collected in a flask of 100 c.c. capacity which contains 10 c.c. of a solution of ammonia (sp. gr. 0·960), and 20 c.c. of $N/10$ silver nitrate solution are added. A small funnel is then placed in the flask, and the mixture heated for an hour in a water-bath; after cooling, it is diluted with water to 100 c.c. To 50 c.c. of the clear filtrate are added 6 c.c. of nitric acid and 1 c.c. of ferric ammonium sulphate solution (1 part of ferric ammonium sulphate to be dissolved as required in a mixture of 8 parts of water and 1 part of dilute sulphuric acid of sp. gr. 1·109-1·114) ; not more than 6·5 c.c. of $N/10$ ammonium thiocyanate solution should then be required to produce a red coloration, which would correspond to at least 0·7 per cent. of allyl mustard oil (1 c.c. of $N/10$ silver nitrate solution $=0·004956$ g. of allyl mustard oil, with ferric ammonium sulphate as the indicator).

B.—GALENICAL PREPARATIONS.

Since the manufacture of galenical preparations has become a branch of industry on a large scale, and is no longer restricted to the pharmacy, methods for their examination have been worked out. This has been rendered necessary by the fact that, as shown in the preceding Section, "Resins, Balsams, and Gum-Resins," the crude materials and drugs used for this purpose are not only subject to great variations, but also occur in commerce of such poor quality that the galenical preparations made from them must naturally be inferior in character. Although the methods for the examination of galenical

[1] *Ber. d. deutsch. pharm. Ges.*, 1898, p. 18.

preparations, such as tinctures and extracts, cannot be regarded as final, they, nevertheless, permit of forming an opinion which is to some extent useful respecting their quality and that of the drugs from which they were made. The methods employed depend upon the observation of such physical characters as transparency, colour, odour, taste, specific gravity, and, when practicable, the quantitative determination of some essential constituent. Such methods of examination have now been incorporated to a large extent in the German Pharmacopœia, whereas the British and United States Pharmacopœias do not as yet describe the physical characters of galenical preparations, and requirements respecting the control of quality or strength are restricted to those preparations of special potency whose active constituents permit of being quantitatively determined.

The following data comprise some of the special methods of examination :—

PAPERS.

Test Papers.

(According to E. Dieterich.)

Sensitiveness.—Ten different strengths of dilute sulphuric acid are prepared, which should contain 1 part of SO_3 in 1000, 5000, 10,000, 20,000, 30,000, 40,000, 50,000, 60,000, 80,000, and 100,000 parts of water respectively, and also ten dilute solutions of ammonia which shall contain NH_3 in the same proportions. The test papers prepared from filter paper are then examined for their sensitiveness by dipping a strip of the paper once in the solutions of sulphuric acid or ammonia, in the order of strength indicated above, and observing with which solution a change of colour takes place.

The test papers prepared from writing paper are examined by placing on them a drop of the above solutions.

The papers should respond to the following limits of sensitiveness :—

Congo Red Paper	.	.	1 : 5000 to 1 : 10,000 SO_3
Curcuma Paper .	.	.	1 : 5000 „ 1 : 10,000 NH_3
Blue Litmus Paper	.	.	1 : 10,000 „ 1 : 40,000 SO_3
Red Litmus Paper	.	.	1 : 10,000 „ 1 : 30,000 NH_3.

Mustard Paper and Mustard Lint.

(According to K. Dieterich and the German Pharmacopœia.)

(a) *Amount of Mustard Flour.*—This is determined by carefully scraping the mustard with a knife from 100 sq. cm. and weighing it.

(b) *Determination of Mustard Oil.*[1]—100 sq. cm. of the mustard

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[1] *Cf.* the determination of essential oil in black mustard seed, under Drugs. Also the determination of mustard oil in mustard flour, by C. Brioux, *Ann. Chim. analyt.*, 1912, 17, 3 ; *J. Soc. Chem. Ind.*, 1912, 31, 148 ; and Greenish and Bartlett, *Pharm. J.*, 1912, 88, 203.

paper, cut in strips, are placed in a flask, and 50 c.c. of water at 20°-25° added. The flask is then corked, allowed to stand for two hours with repeated agitation, 10 c.c. of alcohol and 2 c.c. of olive oil added, and the mixture distilled with careful condensation. The first 30 c.c. which pass over are collected in a flask of 100 c.c. capacity which contains 10 c.c. of a solution of ammonia (sp. gr. 0·960), and 10 c.c. of $N/10$ silver nitrate solution are added. A small funnel is then placed in the flask, and the mixture heated for an hour in the water-bath, when, after cooling, it is diluted with water to 100 c.c. To 50 c.c. of the clear filtrate are added 6 c.c. of nitric acid and 1 c.c. of ferric ammonium sulphate solution; not more than 3·8 c.c. of $N/10$ ammonium thiocyanate solution should then be required to produce a red coloration, which would correspond to at least 0·0119 g. of allyl mustard oil in 100 sq. cm. (1 c.c. of $N/10$ silver nitrate solution = 0·004956 g. of allyl mustard oil, with ferric ammonium sulphate as the indicator).

The mustard paper and mustard lint should conform to the following limits :—

I. *Coarse Flour.*

Coarse Mustard Flour to 100 sq. cm., 2·016-4·551 g.

Mustard oil, calculated on the flour, 0·89-1·57 per cent.

II. *Fine Flour.*

Fine Mustard Flour to 100 sq. cm., 1·50-2·991 g.

Mustard oil, calculated on the flour, 0·80-1·44 per cent.

III. *Mustard Lint.*

Mustard Flour to 100 sq. cm., 2·1-2·711 g.

Mustard oil, calculated on the flour, 1·11-1·21 per cent.

The British Pharmacopœia directs that *Charta Sinapis* (Mustard Plaster) should be prepared by spreading a mixture of 5 g. of equal parts of black and white mustard seed, deprived of fixed oil, with a sufficient quantity of solution of india-rubber, over about 2 sq. dm. of cartridge paper, whilst the United States Pharmacopœia requires of Mustard Paper that a surface of 60 sq. cm. should contain about 4 g. of black mustard, deprived of fatty oil.

PLASTERS.

Plasters having a rubber basis, which are now most largely used in medical practice, should be examined first of all for the amount of caoutchouc they contain.

A method for the determination of caoutchouc has been worked out by K. Dieterich.[1]

[1] "Ueber die quantitative Bestimmung von Kautschuk in Kautschuk-Pflastern," *Pharm. Zeit.*, 1903, No. 78, and the *Helfenberger Annalen*, 1903.

The general method for the examination of plasters consists in the determination of the water. This is effected by heating 1 g. of the respective plaster, contained in a tared, shallow, porcelain dish, in a drying oven at 100°, until the weight remains constant.

The determination of glycerin, which is sometimes carried out, is very uncertain; a reliable method is required before any conclusions can be drawn as to the amount of glycerin present.

LIQUID OR FLUID EXTRACTS.

According to the general method of examination the following points are to be considered:—

(a) *Tests for Identity.*—See the *Helfenberger Annalen*, 1891, pp. 50-80.

(b) *Specific Gravity at* 15°.

(c) *Dry Residue at* 100°.—5 g. of the liquid extract are evaporated in a previously ignited and weighed platinum dish, and the residue dried at 100° until the weight is constant.

(d) *Ash.*—The dry residue is ignited.

(e) *Examination according to the Pharmacopœia.*—The number of liquid extracts adopted by the national pharmacopœias not only varies considerably, but in many cases there are also important differences with respect to their method of preparation, or in the nature of the solvent employed for the extraction of the drug. In accordance with these facts preparations bearing the same name may differ appreciably in character, and in the examination of such products consideration must therefore be taken of the requirements of the particular pharmacopœia to which they are expected to conform. These differences are, moreover, by no means constant, since changes in the method of preparation or in strength are frequently made in successive revisions of a pharmacopœia. The British Pharmacopœia directs the following liquid extracts to be assayed for the proportion of their active constituents:—Belladonna root, cinchona, ipecacuanha, nux vomica, and opium. In the United States Pharmacopœia such requirements are extended to the following fluid extracts:—Aconite, belladonna root, cinchona, coca, colchicum seed, conium, guarana, hydrastis, hyoscyamus, ipecacuanha, nux vomica, pilocarpus, scopola, and strammonium.

A special method is given for the following unofficial preparation:—

Liquid Extract of Kola.

(From unroasted nuts, according to K. Dieterich.)

(a) *Determination of Total Alkaloid.*—20 g. of the liquid extract are evaporated to a syrupy consistency, or until all the alcohol has been removed, and the residue then treated as described under Kola Nuts

(Section IX., Seeds, p. 250). The weight of total alkaloid, multiplied by 5, expresses the percentage.

(b) *Free and Combined Alkaloid.*—20 g. of the liquid extract are evaporated to a syrupy consistency, or until all the alcohol has been removed, and the residue treated as described under Kola Nuts (*b*) (p. 251). By multiplying with 5 the percentage of free caffeine is obtained, and by subtracting the latter from the total alkaloid the percentage of combined caffeine is indicated.

The purification of the caffeine can only be effected by means of acid, since many liquid extracts contain glycerin, from which the caffeine cannot be separated by either water or alcohol.

(c) *Ash*

(d) *Specific Gravity*   } According to the usual methods.

(e) *Residue, dried at* 100°

(f) *Identification.*—The identification of liquid extract of kola may be effected either with the alkaloidal residue obtained, or with the extract itself. In the first case the identification depends upon the purple coloration which caffeine gives with chlorine water and ammonia (the so-called murexide reaction), or, if the extract be used, 20 g. of the liquid are evaporated, the residue triturated with a solution of ammonia, and then shaken with ether. On evaporating the ethereal liquid, a residue will be obtained which, although impure, yields a purple colour with the above reagents.

The figures obtained for the extract should be within the following limits, which will indicate that it has been prepared from the more active unroasted kola nuts :—

Total Caffeine	0·95 to 1·5	per cent.
Free Caffeine	0·110 „ 0·810	„
Combined Caffeine	0·03 „ 1·019	„
Dry Residue	14·0 „ 17·0	„
Ash .	1·04 „ 1·42	„
Specific Gravity at 15°	0·974 „ 0·976.	

THICK EXTRACTS AND DRY EXTRACTS.

In addition to the liquid or fluid extracts the German Pharmacopœia recognises the following three forms of an extract :—

1. *Thin Extracts*, which have a degree of fluidity resembling that of fresh honey ; 2. *Thick Extracts*, which, when cold, do not permit of being poured ; and 3. *Dry Extracts*, which are such as can be powdered. In other pharmacopœias their characters are designated as " soft," " firm," " in powder," of a " pilular consistence," etc.

The general method for the examination of the above-mentioned extracts is, according to E. Dieterich, as follows :—

(a) *Reactions for Identity.*

(b) *Loss on drying at* 100°.—2 g. of the extract are dried at 100° in an ignited and weighed platinum dish until the weight is constant.

(c) *Ash.*—The dried extract is incinerated.

(d) *Examination according to the Pharmacopœia.*—The remarks concerning the variations in liquid or fluid extracts are equally applicable to the so-called solid extracts. Among those recognised by the British Pharmacopœia the following are directed to be assayed for the proportion of active constituent :—Belladonna root, nux vomica, and opium. The United States Pharmacopœia extends these requirements respecting strength to the following extracts :—Belladonna leaves, colchicum corm, hyoscyamus, nux vomica, opium, physostigma, scopola, and strammonium.

TINCTURES.

The class of galenical preparations known as "Tinctures" exhibits not only great variation with respect to the number adopted by the different national pharmacopœias, but also with regard to their mode of preparation and strength. No general standards can therefore be adopted for them, such as those of specific gravity and the amount of dry residue which they yield on evaporation, and the more specific requirements must naturally be in conformity with those of the respective pharmacopœias. The British Pharmacopœia directs the tinctures of belladonna, nux vomica, and opium to be assayed for alkaloid, and the tincture of jalap is required to contain a definite amount of resin ; whereas the United States Pharmacopœia extends these more precise requirements to the tinctures of aconite, belladonna, colchicum seed, hydrastis, hyoscyamus, nux vomica, opium, physostigma, and strammonium.

OINTMENTS.

The British and United States Pharmacopœias restrict their requirements concerning ointments and cerates to the prescribed methods of preparation and strength. The only exception is the more precise requirements of the latter work for the following preparation :—

Mercurial Ointment.

The United States Pharmacopœia directs that the amount of mercury contained in this preparation shall be determined by the following method :[1]—Weigh 10 g. of mercurial ointment in a tared dish, melt it, then remove it from the flame and add 50 c.c. of warm petroleum spirit. Stir the mixture well, allow the mercury to settle completely, and decant the petroleum spirit. Wash the residue with successive portions of 10 c.c. each of warm petroleum spirit until it is entirely free

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[1] For the volumetric determination of mercury in mercurial preparations see Crewe, *Pharm. J.*, 1908, **81**, 359 ; and Cowie, *ibid.*, 1911, **87**, 885.

from fatty matter, carefully retain all the separated mercury in the dish, and allow all traces of the petroleum spirit to evapora.e.   Add to the residue 10 c.c. of dilute hydrochloric acid (10 per cent.), heat gently, and stir with a glass rod until the mercury collects in a globule.   Pour off the acid, warm the mercury with a little distilled water, dry the globule on filter paper, and weigh.   The mercury should weigh not less than 4·9 g.

The corresponding preparation of the British Pharmacopœia (*Unguentum Hydrargyri*) contains about 48·5 per cent. of mercury, while that of the German Pharmacopœia (*Unguentum Hydrargyri cinereum*) contains 30 per cent. of mercury.

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ESSENTIAL OILS

By E. GILDEMEISTER, Ph.D., Leipzig. English translation revised by FREDERICK B. POWER, Ph.D., LL.D., Director of the Wellcome Chemical Research Laboratories, London.

THE examination of essential oils for the purpose of detecting adulterations is conducted partly by physical and partly by chemical methods.

In the first place, by determining the physical properties it is ascertained whether the oil under examination is a normal one. That is the case if all the constants are within the limits adopted for pure oils. The chemical examination, as a rule, affords information regarding the quality of the oil, and by this means the nature and amount of any adulterant present may also be found.

The physical tests comprise the determination of the specific gravity, optical rotatory power, and solubility in alcohol of different strengths, sometimes also the congealing point, boiling point, and amount of residue left on evaporation. The usual adulterants, such as alcohol, fatty oil, petroleum, oil of turpentine, cedar-wood oil, etc., almost always affect one or more of the physical constants, and may thus be detected. For example, oil of turpentine when added to oil of sweet orange diminishes its rotatory power, while the presence of cedar-wood oil in oil of lavender renders the latter insoluble in 70 per cent. alcohol. The adulteration of any essential oil with alcohol causes a decrease in specific gravity, while the addition of petroleum to the oil of star-anise lowers its congealing point and influences its solubility in 90 per cent. alcohol.

The chemical examination of an essential oil is closely connected with its physical tests. If a definite adulteration is suspected, an attempt should be made to isolate the adulterant and to identify it. Even when an oil has been found to be normal, a determination of its quality is frequently desirable, but among the methods subsequently to be described the one to be employed would depend upon the composition of the respective oil. The chief constituents of some oils, and those which determine its value, are alcohols, while in other cases they are esters, aldehydes, phenols or ketones, and by their quantitative determination information is not only obtained with regard to the normal or abnormal character of the oil, but also respecting its quality. Thus, of two unadulterated

lavender oils, that would be considered the better which contains the larger percentage of esters. Cassia oil is valued according to its content of cinnamic aldehyde, caraway oil according to the amount of ketone it contains, and clove oil according to the amount of its phenolic constituent.

DETERMINATION OF THE PHYSICAL CONSTANTS.

Specific Gravity.—When a sufficient quantity of material is available, the specific gravity is most conveniently determined by means of the hydrostatic balance of Mohr or Westphal. If the amount of oil is not sufficient for this method, a pyknometer may be used, the temperature being maintained at 15°.

Optical Rotatory Power.—The rotatory power of essential oils can be determined in any polarising apparatus which is adapted for sodium light; the half-shadow apparatus of Laurent is especially to be recommended. In the case of dark oils, short observation tubes having a length of 50 and 20 mm. may be used, in order to avoid dilution with a solvent. The angle of rotation, which is directly observed in a 100 mm. tube, is designated as a, and the specific rotatory power [1] as $[a]_D$, which is calculated according to the formula $[a]_D = \dfrac{a}{l \cdot d}$. In this formula l denotes the length of the tube in millimetres, and d the specific gravity of the liquid. In general, it is not necessary to maintain a definite temperature, but with some oils, such as those of lemon and sweet orange, the determination is conducted at 20°.

Solubility.—For the customary determination of the solubility of essential oils, alcohol of 70, 80, and 90 per cent. by volume is chiefly employed. To 1 c.c. of the oil, in a small graduated cylinder, alcohol of a definite strength is added, drop by drop, until solution is effected. In most cases the liquid will remain clear when further amounts of the solvent are added, but sometimes an opalescent turbidity will subsequently appear, even with pure oils. If the oil under examination contains petroleum, this will separate on the surface of the liquid in drops after standing for a time, whereas fatty oil will collect at the bottom of the vessel. Cedar-wood oil, copaiba oil, and gurjun oil, as well as oil of turpentine, are quite sparingly soluble in alcohol, and are indicated by this property when they have been added with a fraudulent purpose to other more readily soluble oils.

Congealing Point.—The apparatus employed in the laboratory of Schimmel & Co.[2] for determining the congealing point of essential oils,

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[1] *Cf.* H. Landolt, *Das optische Drehungsvermögen organischer Substanzen*, 2nd Edition, 1898. English translation by J. H. Long, *The Optical Rotating Power of Organic Substances and its Practical Applications*, 1902.

[2] Semi-annual Report of Schimmel & Co., October 1898, p. 43.

such as those of anise, star-anise, and fennel, is adapted from the well-known apparatus of Beckmann for determining molecular weights by the depression of the freezing point, and has the form represented in Fig. 46.

The battery jar A serves as a receptacle for the cooling liquid or freezing mixture. The glass tube B suspended from the metal cover forms an air-jacket around the freezing tube C, and prevents the premature solidification of the oil to be tested. The freezing tube C is wider at the top, and becomes narrower at the place where it rests on the rim of the tube B. In order to retain C in a fixed position, three glass supports are fastened on the inside of the tube B, about 5 cm. below its upper edge. The thermometer, which is graduated in $\frac{1}{2}$ degrees, is securely held by three springs in a metal disc, which permit of sliding it up or down.

To carry out a determination with anise or star-anise oil the battery jar is filled with cold water and pieces of ice, but for fennel oil a freezing mixture prepared from ice and salt is used. So much of the oil to be examined is then brought into the freezing tube as to have a height of about 5 cm., and the thermometer is immersed in the liquid without allowing it to touch the sides of the glass at any point. During the process of cooling, the super-cooled oil is protected from any disturbance which would cause its premature solidification. If the temperature has sunk to about 5°· below the congealing point, that is, with anise oil to 12°, with star-anise oil to 10°, and with fennel oil to 3°, crystallisation is induced by rubbing or scratching the sides of the glass with the thermometer. If this procedure is not successful, a

FIG. 46.

small crystal of the congealed oil or a little solid anethol is brought into the liquid, when solidification will ensue with a considerable development of heat. The solidification may be accelerated by constant stirring with the thermometer, when the temperature will rise rapidly, and finally attain a maximum, which is termed the "congealing point" of the oil.

If such an apparatus as the above is not available, the determination can be conducted in an ordinary flask, which is cooled by placing it in a freezing mixture, provided the amount of oil is not too small, that is, not less than 100 g.

Fractional Distillation.—Fractional distillation is employed when it
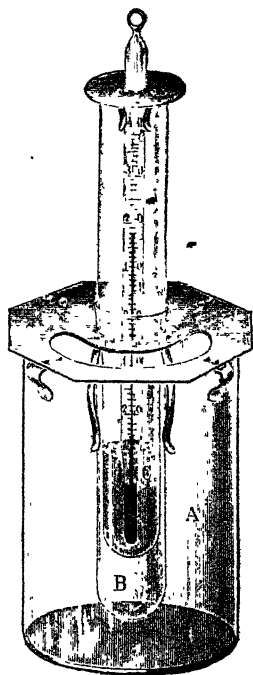
is a question of isolating a definite constituent of an oil or of separating individual portions from each other. For a scientific examination it is necessary to subject the oil to repeated fractional distillation, with the aid of a fractionating column, in order to separate the constituents of different boiling point, and even then the separation is sometimes very incomplete. In testing for adulterants, fractional distillation will frequently effect the isolation of the adulterating agent, such as alcohol, petroleum, oil of turpentine, and other liquids. Lemon oil, rose‑mary oil, and oil of spike are tested for turpentine oil by distilling over 10 or 50 per cent. of the respective oil, and determining the rotatory power of the distillate. In order to obtain concordant results by this method, distillation flasks of uniform size must be used, and the fractionation so conducted that the distillate passes over drop by drop.

FIG. 47.

The Ladenburg fractionating flask, which is used in the laboratory of Schimmel & Co.[1] for testing the three above‑mentioned oils, has the shape and size indicated in Fig. 47.

The statements regarding boiling point in this Section refer to determinations in which the mercurial column of the thermometer is entirely in the vapour of the liquid.

CHEMICAL METHODS OF EXAMINATION.

Determination of the amount of Esters by Saponification.

The esters of the alcohols $C_{10}H_{18}O$ and $C_{10}H_{20}O$, on account of their pleasant odour, represent some of the most valuable constituents of essential oils. Linalyl acetate is the chief odorous component of the oils of bergamot, petit-grain, and lavender; bornyl acetate imparts to the pine-needle oils their characteristic aroma; menthyl acetate occurs in peppermint oil, and other examples might be given. All these esters are readily saponified by an alcoholic solution of potassium hydroxide, and may thus be determined quantitatively, in fact, in the same manner as is customary in the analysis of fats.

These methods of examination include the determination of the acid

[a] Semi-annual Report of Schimmel & Co., October 1898, p. 41.

value (A.V.), ester value (E.V.), and saponification value (S.V.). The acid value expresses how many milligrams of potassium hydroxide are necessary for neutralising the free acid contained in 1 g. of oil. The ester value denotes the number of milligrams of potassium hydroxide required to saponify the esters contained in 1 g. of oil. The saponification value designates the sum of the acid and ester values. Since the essential oils usually contain but very little free acid, this determination can generally be neglected.

The saponification is conducted in a small, wide-necked flask of potash glass, having a capacity of 100 c c. A glass tube, about 1 m. in length, which is inserted in a perforated stopper, will serve as a reflux condenser. In such a flask about 2 g. of the oil are weighed accurately to 1 cg. and 10-20 c.c. of $N/2$ alcoholic solution of potassium hydroxide added ; in most cases 10 c.c. of $N/2$ potassium hydroxide solution are sufficient, but with some oils having a high ester content, such as Roman chamomile and wintergreen oils, 30 c.c. must be used. The oil should, however, first be tested for free acid, after the addition of a little alcoholic solution of phenolphthalein. The flask, with the attached condenser, is then heated on a steam-bath for half an hour to one hour, after which the cooled contents of the flask are diluted with about 50 c.c. of water, and the excess of alkali titrated with $N/2$ sulphuric acid. In order to saponify menthyl and bornyl *iso*valerates completely, they must be boiled for two to three hours with a considerable excess of alkali.

In order to calculate from the saponification value found the amount of linalyl, geranyl, or bornyl acetate ($C_{10}H_{17}O.COCH_3$. molec. wt. = 196) contained in an oil, the following equation is employed :—

$$\frac{196 \times S.V.}{560} = \text{percentage of ester.}$$

In the case of acetic esters of alcohols such as menthol, citronellol, etc. ($C_{10}H_{19}O.COCH_3$. molec. wt. = 198), the percentage of esters is expressed by the equation: $\dfrac{198 \times S.V.}{560}$.

In order to ascertain the amount of alcohols of the formulæ $C_{10}H_{18}O$ (molec. wt. = 154), $C_{10}H_{20}O$ (molec. wt. = 156), and $C_{15}H_{24}O$ (molec. wt. = 220) respectively, the following equations are used :—

$$\frac{154 \times S.V.}{560}, \quad \frac{156 \times S.V.}{560}, \text{ and } \frac{220 \times S.V.}{560}.$$

Determination of the amount of free Alcohols by Acetylation.

The alcohols of the formulæ $C_{10}H_{18}O$, $C_{10}H_{20}O$, and $C_{15}H_{24}O$ respectively, which occur as esters in essential oils, are also frequently met with in the free state ; for example, borneol, geraniol, terpineol, linalool,

thujyl alcohol, menthol, citronellol, and santalol. For their quantitative determination advantage is taken of their property of becoming converted into acetic esters by heating with acetic anhydride, in accordance with the equation :—

$$C_{10}H_{18}O + (CH_3CO)_2O = C_{10}H_{17}O . COCH_3 + CH_3CO_2H.$$
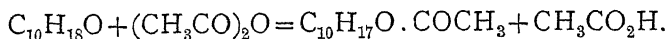
This change only takes place quantitatively in the case of borneol, geraniol, menthol, citronellol, and santalol. Linalool and terpineol, on the other hand, become partially decomposed on heating with acetic anhydride, with the elimination of water. For the purpose of a quantitative acetylation,[1] 10 c.c. of the oil, together with an equal volume of acetic anhydride and about 2 g. of anhydrous sodium acetate, are brought into a small flask provided with a ground-glass condensing tube (Fig. 48), and the mixture maintained in a uniform state of ebullition for one hour. After cooling, some water is added to the contents of the flask, which is then heated for a quarter of an hour on a water-bath in order to decompose the excess of acetic anhydride. By means of a separating funnel, the aqueous, acid liquid is subsequently drawn off from the oil, and the latter washed with water, or preferably with a solution of common salt, until the washings are neutral.
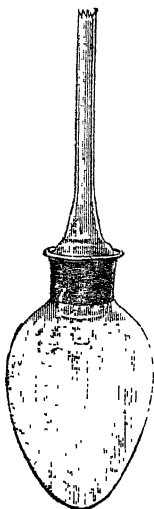
FIG. 48.

After having been dried with anhydrous sodium sulphate, 2 g. of the acetylated oil are saponified according to the method described above (p. 263). From the ester value thus found, the corresponding amount of the alcohol contained in the original oil is calculated, according to the following equations :—

1. Percentage of alcohol $C_{10}H_{18}O$ in the original oil $= \dfrac{a \times 15.4}{s - (a \times 0.042)}$.

2. Percentage of alcohol $C_{10}H_{20}O$ in the original oil $= \dfrac{a \times 15.6}{s - (a \times 0.042)}$.

3. Percentage of alcohol $C_{15}H_{24}O$ in the original oil $= \dfrac{a \times 22.0}{s - (a \times 0.042)}$.

In these formulæ a designates the number of c.c. of $N/1$ potassium hydroxide solution used, and s the amount of acetylated oil employed for saponification, expressed in grams.

Aldehyde Determination by the Bisulphite Method of Schimmel & Co.

This method depends upon the property of some aldehydes of forming compounds with sodium bisulphite which are soluble in water.

[1] Semi-annual Report of Schimmel & Co., October 1894, p. 62.

If oils rich in aldehyde, such as cassia oil, Ceylon cinnamon oil (cinnamic aldehyde), or lemon-grass oil (citral) be shaken with a hot, concentrated solution of sodium bisulphite, the total aldehyde will pass into the aqueous solution, whilst the other constituents of the oil, being insoluble in water, will float on the surface. The diminution in volume of the oil by this process corresponds to its content of aldehyde.

For such a determination a special glass flask[1] (cassia flask or aldehyde flask, Fig. 49) of about 100 c.c. capacity is used. This has a neck about 13 cm. in length, 8 mm. inside diameter, and is graduated in $\frac{1}{10}$ c.c. The neck has a capacity of somewhat more than 6 c.c., and the zero of the scale is a little above the junction of the body of the flask and the neck.

By means of a pipette, exactly 10 c.c. of oil are brought into the flask, the same amount of an approximately 30 per cent solution of sodium bisulphite added, the mixture shaken, and the flask then placed in a bath of boiling water. After the curdy mass which is first formed has liquefied, so much bisulphite solution is gradually added, while being constantly heated in the water-bath and frequently shaken, that the flask becomes at least three-quarters filled. The heating is then continued for some time, or until no more solid particles float in the liquid, and there is a layer of clear oil on the surface of the salt solution, while the odour of the aldehyde has disappeared. After cooling, the flask is filled with bisulphite solution, so that the oil rises in the neck, and the lower boundary of the oily layer is exactly in line with the zero mark on the neck

Fig. 49.

of the flask. The number of cubic centimetres of non-aldehydic constituents is then read off on the scale, and by subtracting this from 10 the aldehyde content is found.
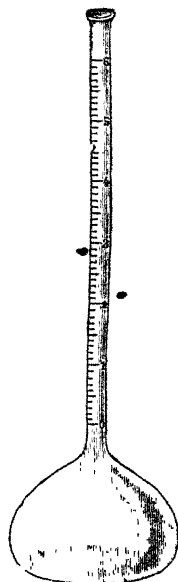
This method can only be somewhat accurately employed for oils which are relatively rich in aldehyde, such as cassia oil, cinnamon oil, and lemon-grass oil. It is quite inadequate for lemon oil, which contains but small amounts (5-8 per cent.) of aldehyde.

Determination of Aldehydes and Ketones with Neutral Sulphite,
according to Burgess (The Sulphite Method).

In place of the acid sulphite, neutral sodium sulphite may also be used in the cassia flask for the quantitative determination of citral and cinnamic aldehyde. Even the ketones, carvone and pulegone, may

[1] Semi-annual Report of Schimmel & Co., October 1890, p. 18.

be determined in the same manner, which is not possible by the method above described.

The determination is conducted in the following manner :—5 c.c. of the oil are brought into a cassia flask, together with a saturated solution of sodium sulphite, and, after the addition of two drops of a phenolphthalein solution, the mixture is heated in a water-bath, with frequent agitation. The sodium hydroxide which is liberated by this reaction is neutralised from time to time with dilute acetic acid (1 : 5) or with sodium bicarbonate, until a red coloration no longer appears on further heating. The oil then is brought into the neck by filling the flask with water, and, after cooling, its volume may be accurately determined. The amount of oil absorbed, multiplied by 20, gives the percentage content of aldehyde or ketone.

S. Sadtler[1] has proposed to determine volumetrically the sodium hydroxide liberated by the action of aldehydes or ketones, with the use of rosolic acid as the indicator, and thus to calculate the amount of aldehyde or ketone in the oil. This method, however, fails in practice, owing to the impossibility of determining the end reaction with precision.

Determination of Phenols.

For an approximately accurate determination, a measured quantity of the oil to be examined is shaken with a dilute (not more than 5 per cent.) solution of sodium hydroxide. The diminution in volume of the oil indicates the amount of phenols present. For this purpose a burette of 60 c.c. capacity is filled to the 10 c.c. mark with a 5 per cent. solution of sodium hydroxide. 10 c.c. of the oil to be examined are then brought upon the surface of the liquid, the burette closed with a tightly fitting cork, and, after shaking the mixture vigorously, allowed to stand for twelve to twenty-four hours. Any drops of oil which may adhere to the sides of the glass are detached by tapping or inclining the burette. When the alkaline liquid has become clear, the amount of non-phenolic constituents of the oil can be read off.

The cassia flask described on p. 265 can also be used for phenol determinations in place of a burette.

Detection of Alcohol.

The adulteration of an essential oil with alcohol, which is of frequent occurrence, is indicated in the first place by a low specific gravity.

When drops of an oil containing alcohol are allowed to fall into water, they will not remain clear and transparent as in the case of a pure oil, but will appear opaque or show a milk-like turbidity.

In order to separate and identify the alcohol, the suspected oil is

[1] *J. Soc. Chem. Ind.*, 1904, 23, 303.

heated until it begins to boil, the first few drops of the distillate collected in a test tube, and then passed through a filter which has been moistened with water, so as to remove any drops of oil which may have been mechanically carried over. After the filtered liquid has been made strongly alkaline with a dilute solution of potassium hydroxide, and heated to 50°-60°, a solution of iodine in potassium iodide is added until a permanent yellow coloration is produced. If alcohol be present, small crystals of iodoform will be deposited after a time at the bottom of the liquid. It is, however, to be borne in mind that acetone and ethyl acetate, as well as the lower aldehydes, will give the iodoform reaction under the same conditions.

If a measured quantity of an oil containing alcohol be shaken in a graduated cylinder with water, the increase in volume of the aqueous layer will correspond approximately to the amount of alcohol present. The alcohol can then be separated from the water by distillation, and identified as described above.

The amount of alcohol in an adulterated oil may also be determined by a comparison of the specific gravity of the oil before and after shaking with water.

Detection of Fatty Oil.

If an essential oil is adulterated with a fatty oil, it does not yield a clear solution with considerable amounts of 90 per cent. alcohol, and leaves a permanent greasy stain when evaporated on writing paper. It is to be borne in mind, however, that the essential oils obtained by expression, such as those of bergamot, lemon, and sweet orange, produce similar permanent stains on paper; but these oils are soluble in 90 per cent. alcohol, and the stain is not caused by fatty oil. For the detection of the fatty oil, the essential oil is either distilled over with steam, or evaporated on a water-bath. The residue, when it consists of fat, will be insoluble in 70 and 90 per cent. alcohol (only ricinus oil is soluble in 90 per cent. alcohol, but it is insoluble in 70 per cent. alcohol); it will give off the irritating vapours of acrolein when heated in a test tube with acid potassium sulphate, and will be saponified by an alcoholic solution of potassium hydroxide, giving a saponification value between 180 and 200.

Detection of Mineral Oil.

Petroleum, mineral oil, or fractions of the latter, are practically insoluble in alcohol, even of the highest strength, and they are, therefore, easily detected in essential oils. An essential oil which is adulterated with a mineral oil will yield a turbid mixture when shaken with 90 per cent. alcohol, but this will soon become clear on standing, and the separated mineral oil will then float on the surface of the alcohol. The mineral oil, when repeatedly washed with alcohol, will be

recognised as such by its permanence towards a solution of potassium hydroxide, as also towards concentrated sulphuric and nitric acids.

Detection of Turpentine Oil.

The most frequently observed adulteration of essential oils consists in an addition of turpentine oil. Those oils which in a pure state contain no pinene—the chief constituent of oil of turpentine—may be examined for an adulteration with the latter by repeated fractional distillation and the isolation of the respective hydrocarbon. The portion distilling at about 160° is separately collected, and the pinene identified by its characteristic derivatives, for which purpose the nitrosochloride and the bases prepared therefrom, pinene nitrolbenzyl-amine or pinene nitrolpiperidine, are best adapted.

According to the directions given by Ö. Wallach,[1] 50 g. each of the respective fraction, glacial acetic acid, and ethyl nitrite (or amyl nitrite) are well cooled in a freezing mixture, and to the mixture of the three substances 15 c.c. of crude (33 per cent.) hydrochloric acid are gradually introduced. The nitrosochloride soon separates in a crystalline form, and when drained at the pump and washed with cold alcohol is obtained sufficiently pure for further treatment. A portion of the nitrosochloride is hydrolysed with a solution of potassium hydroxide and converted into nitrosopinene,[2] melting at 132°. To another portion an excess of an alcoholic solution of benzylamine or piperidine is added,[3] the mixture heated for a short time on the water-bath, and the nitrolamine thus produced separated by the addition of water. The melting point of pinene nitrolpiperidine is 118°-119°, that of pinene nitrolbenzylamine, 122°-123°.

In those cases in which pinene is a natural constituent of an essential oil, an adulteration with turpentine oil may be recognised by a change in its physical constants, such as specific gravity, solubility, and rotatory power. With regard to the optical behaviour, it should be noted that there are both dextrorotatory and lævorotatory turpentine oils.

CONSTANTS AND PROPERTIES OF SOME ESSENTIAL OILS OF COMMERCIAL AND INDUSTRIAL IMPORTANCE.[4]

Anise Oil.—From the fruits of *Pimpinella Anisum*, Linné.

$d^{20°}$ 0·980-0·990; a_D lævorotatory to $-1°$ 50′ (an oil to which fennel oil or fennel stearoptene has been added is dextrorotatory); soluble in

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[1] *Annalen*, 1888, **245**, 251, and 1889, **253**, 251. [2] Wallach and Lorentz, *ibid.*, 1891, **258**, 198.
  [3] Wallach, *ibid.*, 1888, **245**, 253.; 1889, **252**, 130.
  [4] Since it is not expedient to enumerate all the essential oils, reference may be made to the comprehensive work: *Die ætherischen Oele*, by E. Gildemeister and Fr. Hoffmann. This contains more detailed information respecting their origin, preparation, composition, and commercial varieties.

$1\frac{1}{2}$-3 vols. of 90 per cent. (by volume) alcohol; congealing point (see p. 260) $+17°$ to $+19°$. When improperly kept the congealing point may become depressed to below $0°$, and at the same time the oil will become heavier than water through the formation of anisaldehyde.

Anethole, $C_{10}H_{12}O$.—$d^{25°}$ 0.984-0.986; $a_D \pm 0°$; $n_D{}^{25°}$ 1.559-1.561; congealing point $21°$-$22°$; melting point $22.5°$-$23°$; boiling point (760 mm.) $233°$-$234°$; soluble in 2-3 vols. of 90 per cent. alcohol.

Bay Oil.—From the leaves of *Pimenta acris*, Wight.

$d^{15°}$ 0.965-0.985; a_D lævorotatory to $-3°$. Usually not giving a clear solution with 90 per cent. alcohol. Eugenol content 40-70 per cent. The determination of the eugenol is conducted in the manner described under Clove Oil.

Bergamot Oil.—The oil expressed from the rind of the fruit of *Citrus Bergamia*, Risso.

Colour green or yellowish-brown; $d^{15°}$ 0.881-0.886; $a_D + 8°$ to $+24°$; soluble in $\frac{1}{2}$ vol. or more of 90 per cent. alcohol. Amount of linalyl acetate (see p. 262) 35-45 per cent.; residue on evaporation, 5-6 per cent. For determining the latter, about 5 g. of the oil are weighed accurately to 1 cg. in a tared glass dish, and heated on a water-bath until the residue has completely lost the odour of bergamot oil. After cooling, the dish is weighed with the residue. This will amount to more than 6 per cent. of the oil if fatty oil were present. Rectified bergamot oil is colourless, and volatilises without leaving any appreciable residue.

Bitter Almond Oil.—Prepared by the fermentation and subsequent distillation of bitter almonds, from *Prunus Amygdalus*, Stokes, or of apricot kernels, from *Prunus Armeniaca*, Linné, which have been deprived of fatty oil.

Bitter Almond Oil containing Hydrocyanic Acid.—$d^{15°}$ 1.045-1.070, but with a large proportion of hydrocyanic acid the specific gravity is higher; a_D inactive or nearly so; soluble in 1-2 vols. of 70 per cent. alcohol.

Bitter Almond Oil deprived of Hydrocyanic Acid.—$d^{15°}$ 1.050-1.055; boiling point $179°$. In order to distinguish this oil from one containing hydrocyanic acid, 10-15 drops of the respective oil are shaken with 2-3 drops of an approximately 30 per cent. solution of sodium hydroxide, or a corresponding amount of more dilute alkali. After the addition of a few drops of a partially oxidised ferrous sulphate solution, the mixture is again shaken, and then acidified with dilute hydrochloric acid, when the precipitate of ferroso-ferric oxide will be dissolved, and, if hydrocyanic acid be present, the characteristic blue precipitate of prussian blue will be formed.

For the quantitative determination of hydrocyanic acid in essential oils various volumetric methods have been proposed, some of which,

however, give very poor results.   The following gravimetric method has been found most trustworthy :—About 1 g. of the oil is accurately weighed, dissolved in ten to twenty times its amount of alcohol, and 10 g. of a chlorine-free, alcoholic solution of ammonia added.   After standing for a time, an aqueous solution of 1 g. of silver nitrate is added, and the mixture then acidified with nitric acid.   When the liquid has become clear, the silver cyanide is collected on a dried and weighed filter, thoroughly washed with water, and dried at 100° until the weight is constant.

The silver precipitate thus obtained contains the entire amount of hydrocyanic acid present in the oil, whereas without the preceding treatment with ammonia, which decomposes the mandelic nitrile, only a part of the hydrocyanic acid would be determined.

Detection of Chlorine.—Synthetic bitter almond oil prepared from benzyl chloride or benzylidene chloride, is more or less contaminated with chlorinated products.   Since synthetic benzaldehyde is much used to adulterate true bitter almond oil, its presence can be ascertained by the detection of chlorine.   Synthetic cinnamic aldehyde likewise sometimes contains chlorine, and the detection of chlorine in cinnamon oil is similarly evidence of its adulteration with the synthetic aldehyde. It should specially be noted, however, that synthetic benzaldehyde and cinnamic aldehyde which are free from chlorine now also occur in commerce.

For the detection of chlorine a piece of filter paper 5 × 6 cm. in size is folded in the form of a taper, soaked in the oil to be examined, and the excess of oil thrown off by two short shakings with the hand.   The paper thus prepared is brought into a small porcelain dish, which is placed in a larger one of about 20 cm. diameter, and lighted by a flame. A beaker of about 2 litres capacity, which has been moistened on the inner surface with distilled water and kept ready for the purpose, is then quickly inverted over the burning taper.   The gaseous products of combustion condense on the moist walls of the beaker, and are washed with 10 c.c. of distilled water on to a filter.   The filtrate should give no turbidity, much less a precipitate of silver chloride, on the addition of a solution of silver nitrate.   The genuine oil, that is, such as has been distilled from bitter almonds or from peach kernels, never gives a reaction for chlorine.

The above-described method of testing the oil has proved to be infallible.   In order, however, to be certain of the result, a control test should always be made with a pure distilled oil, since an incorrect opinion might be formed if the water and the vessels employed were not perfectly free from chlorides.

Caraway Oil.—From the fruits of *Carum Carvi*, Linné.

$d^{15°}$ 0·907-0·915 ; a_D +70° to +80° ; soluble in 3-10 vols. of 80 per

cent., or 1 vol. of 90 per cent. alcohol. Carvone content 50-60 per cent. (to be determined according to the sulphite method described on p. 265).

Carvone (Carvol), $C_{10}H_{14}O$.—$d^{15°}$ 0·964-0·966; boiling point 229°-230°; α_D +57° to +60°; soluble in 16-20 vols. of 50 per cent. alcohol at 20° or in ½-2 vols. of 70 per cent. alcohol; $n_D^{20°}$ 1·497-1·500.

Cassia Oil, Chinese Cinnamon Oil.—From the leaves of the Chinese cinnamon, *Cinnamonum Cassia*, Blume.

$d^{15°}$ 1·055-1·070; optically inactive or slightly lævo- or dextro-rotatory; soluble in 2-3 vols. and more of 70 per cent alcohol, usually with opalescence. Cinnamic aldehyde content (see p. 264) 75-90 per cent. The residue obtained by distillation from a fractionating flask with a low side tube amounts to 6-8, or, at the most, 10 per cent. This residue should be pasty, but not hard or brittle, as would be the case if the oil were adulterated with colophony. Such an addition to the oil may also be detected in the following manner:—To a solution of 1 vol. of cassia oil in 3 vols. of 70 per cent. alcohol is added, drop by drop, an amount up to ½ vol. of a freshly prepared solution of lead acetate in 70 per cent. alcohol, which has been saturated at the room temperature. If a precipitate is produced, it indicates the addition of colophony.

Cinnamon Oil, Ceylon.—From the bark of *Cinnamonum zeylanicum*, Breyne.

$d^{15°}$ 1·023-1·040; α_D lævorotatory to −1°; soluble in 2-3 vols. of 70 per cent. alcohol; cinnamic aldehyde content 65-75 per cent., as determined by the bisulphite method (see p. 264).

Citronella Oil.—From the herb of *Cymbopogon Nardus*, Stapf.

There are two sorts of this oil, the Ceylon and the Java, the latter being the more valuable.

Ceylon Citronella Oil.—$d^{15°}$ 0·900-0·920; α_D lævorotatory to −21°. It should yield a clear solution with 1-2 vols. of 80 per cent. alcohol, and with 10 vols. of this solvent should give a solution which is at most opalescent, but which, on standing, should separate no drops of oil (Schimmel's Test). The oil should also meet these requirements after the addition of 5 per cent. of Russian petroleum (Stricter Schimmel's Test). The apparent amount of alcohol, $C_{10}H_{18}O$ (geraniol+citronellal), as determined by acetylation, at least 57 per cent. (for method of determination see p. 263).

Java Citronella Oil.—$d^{15°}$ 0·886-0·900; α_D lævorotatory to −5°; soluble in 1 or 1·2 vols. of 80 per cent. alcohol. Amount of alcohols, $C_{10}H_{18}O$, usually more than 80 per cent.

Clove Oil.—From the dried flower-buds of *Eugenia caryophyllata*, Thunberg.

$d^{15°}$ 1·044-1·070; α_D lævorotatory to −1° 15′; soluble in 1-2 vols.

of 70 per cent. alcohol. Eugenol content 80-90 per cent. and more.

Clove Stem Oil is distilled from the stems of cloves. $d^{15°}$ 1·040-1·065 ; optical rotation and solubility the same as clove oil. Eugenol content 85-95 per cent.

The determination of the eugenol is conducted either in a cassia flask (Fig. 49, p. 265), with a 3 per cent. solution of sodium hydroxide, or according to Thoms' improved method,[1] which also permits of determining the eugenol contained in the oil in the form of ester.

This method is carried out as follows:—To 5 g. of clove oil are added 20 g. of a solution of sodium hydroxide (15 per cent.), and the mixture gently heated on a water-bath for half an hour, when a layer of sesquiterpene separates on the surface of the liquid. The contents of the beaker, while still warm, are brought into a small separator with a short discharge tube, and the eugenol-sodium solution, which soon settles well, returned to the beaker. The sesquiterpene which remains in the separator is washed twice with a 15 per cent. solution of sodium hydroxide, using 5 c.c. each time, and these washings added to the eugenol-sodium solution. To this solution 6 g. of benzoyl chloride are added, and the mixture shaken, whereby the formation of benzoyl-eugenol is at once effected, with the development of considerable heat. The last portions of unattacked benzoyl chloride are decomposed by heating for a short time on the water-bath. After cooling, the liquid above the solidified ester is removed by filtration, any small crystals which may have got on to the filter being washed with 50 c.c. of water into the beaker, and the mixture heated until the crystalline cake again forms an oil. After gentle agitation it is again allowed to cool, the supernatant clear liquid removed by filtration, and the cake, previously melted, washed twice in the same manner as before with water, using 50 c.c. each time. To the benzoyleugenol, while still moist, 25 c.c. of alcohol (90 per cent. by weight) are immediately added, and the mixture heated on a water-bath, with gentle agitation, until solution is effected. After removing the beaker from the water-bath, the agitation of the contents is continued until the benzoyleugenol separates in the form of small crystals, which takes place within a few minutes. It is then cooled to a temperature of 17°, the precipitate brought on a filter of 9 cm. diameter, and the filtrate allowed to flow into a graduated cylinder, in which it may occupy a space of about 20 c.c. The alcoholic solution which may still be retained by the crystalline magma on the filter is displaced by the addition of so much alcohol (90 per cent. by weight) that the entire filtrate amounts to 25 c.c. The filter with the precipitate, while still moist, is transferred to a weighing tube, previously dried with the filter at 101° and weighed, and the whole heated at 101°

[1] *Arch. Pharm.*, 1903, **241**, 592.

until the weight is constant. At 17° the amount of pure benzoyleugenol dissolved by 25 c.c. of 90 per cent. alcohol is 0·55 g., and this weight must therefore be added to that of the quantity found.

If a designates the amount of benzoic ester found, b the amount of clove oil used (approximately 5 g.), and if 25 c.c. of alcoholic solution are filtered from the ester under the above-mentioned conditions, then the percentage of eugenol in the clove oil is found according to the following formula :—

$$\frac{4100(a+0\cdot55)}{67 \cdot b}.$$

This formula is derived from the two equations :—

Benzoyleugenol   *Eugenol*

$$268 \quad : \quad 164 = (a+0\cdot55): \text{the amount of eugenol found.}$$

$$\text{Eugenol} = \frac{164 \cdot (a+0\cdot55)}{268}.$$

$$\text{Therefore, } b : \frac{164(a+0\cdot55)}{268} = 100: x$$

$$x = \frac{1\cdot64(a+0\cdot55) \cdot 100}{268 \cdot b} = \frac{4100(a+0\cdot55)}{67 \cdot b}.$$

Eucalyptus Oil.—From the leaves of *Eucalyptus globulus*, Labillardière.

$d^{15°}$ 0·910-0·930; a_D +1° to +15°; soluble in 2-4 vols. of 70 per cent. alcohol. An adulteration with the less valuable lævorotatory oil of *Eucalyptus amygdalina*, Labill., which consists almost entirely of phellandrene, $C_{10}H_{16}$, is tested for by adding to the oil, diluted in a test tube with twice its volume of light petroleum, a concentrated, aqueous solution of sodium nitrite. If now acetic acid be added in small portions, phellandrene nitrite will separate in a flocculent form in case this hydrocarbon be present.

In order to determine quantitatively the cineol,[1] the most important constituent of eucalyptus oil, 100 c.c. of the latter are distilled from the Ladenburg fractionating flask, described on p. 262, in such a manner that about one drop passes over per second. In the fraction boiling between 170° and 190°, after diluting it with an equal volume of turpentine oil, the cineol content is determined in the following manner:—To 10 c.c. of the mixture, consisting of the respective fraction and turpentine oil, and contained in a cassia flask of 100 c.c. capacity (p. 265), is added so much of a 50 per cent. resorcinol solution that the flask is about four-fifths filled. The mixture is then vigorously shaken for five minutes, after which the portions of oil which have not entered into the reaction are brought into the neck of the flask by

[1] Semi-annual Report of Schimmel & Co., October 1907, p. 47, and April 1908, p. 50. *J. Soc. Chem. Ind.*, 1908, **27**, 90.

filling the latter with the resorcinol solution. As soon as the liquid has become perfectly clear, or nearly so, which usually requires several hours, the volume of unchanged oil is read off. Any drops of oil which may remain attached to the sides of the vessel are brought to the surface by a frequent rotation and tapping of the flask, and the amount of cineol thus determined is calculated to its percentage by volume in the original oil. The cineol content of good *Eucalyptus globulus* oils should be from 55-80 per cent.

This method depends upon the property of cineol of forming an addition product with resorcinol which is soluble in water.

Eucalyptol (*Cineol*), $C_{10}H_{18}O$.—$d^{15°}$ 0.928-0.930 ; $a_D \pm 0°$; boiling point 176°-177° ; $n_D^{20°}$ 1.458 ; melting point between $+1°$ and $+1.5°$.

Fennel Oil.—From the fruits of *Fœniculum vulgare*, Miller.

$d^{15°}$ 0.965-0.977 ; $a_D + 12°$ to $+18°$, rarely higher ; soluble in 5-8 vols. of 80 per cent. alcohol (sometimes with turbidity), and in 1 vol. of 90 per cent. alcohol. Congealing point (see p. 260), not below $+5°$.

Geranium Oil.—From the leaves of different species of *Pelargonium*. (Palmarosa oil is also incorrectly designated as Turkish or Indian geranium oil).

$d^{15°}$ 0.890-0.907 ; $a_D -6°$ to $-16°$; acid value 3-12 ; ester value 42-78 ; soluble in 3 vols. of 70 per cent. alcohol, sometimes with separation of a paraffin hydrocarbon.

Lavender Oil.—From the flowers of *Lavandula officinalis*, Chaix.

$d^{15°}$ 0.883-0.895 ; $a_D -3°$ to $-9°$; soluble in 3 vols. of 70 per cent. alcohol ; linalyl acetate content 30-55 per cent. and more (for method of determination, see p. 262).

The requirements of the German tax commissioners for a lavender oil which is to be used for denaturing purposes, but which are not sufficient for differentiating between adulterated and pure oils, are as follows :—The density of lavender oil at 15° should be between 0.880 and 0.900 ; 10 c.c. of lavender oil at 20° should yield a clear solution with 30 c.c. of spirit containing 63 per cent. by weight of alcohol.

Lemon Oil.—Obtained by expression from the rind of the fruit of *Citrus Limonum*, Risso.

$d^{15°}$ 0.857-0.861 ; $a_D +58°$ to $+65°$ at 20° ; soluble with turbidity in 90 per cent. alcohol, but giving a clear solution with absolute alcohol. Residue on evaporation 2.5-3.5 per cent. (the method of determination is described under Bergamot Oil, p. 269). Among the numerous published methods for the determination of the citral content none has proved satisfactory.

Lemon-grass Oil.—From the herb of *Cymbopogon flexuosus*, Stapf.

$d^{15°}$ 0.895-0.905 ; a_D dextro- or lævorotatory $+1°$ to $-5°$; soluble in 2-3 vols. of 70 per cent. alcohol, but occasionally showing a slight

turbidity by a further addition of the solvent. Citral content, determined by the bisulphite method (p. 264), 70-85 per cent., by the sulphite method (p. 265), 65-80 per cent. In reporting on the citral content it should be stated which method has been used for its determination.

Citral, $C_{10}H_{16}O$.—$d^{15°}$ 0·892-0·895 ; $\alpha_D \pm 0°$; $n_D 20°$ 1·4880-1·4886 ; boiling point 228°-229°.

Linaloë Oil.—From the wood of different species of *Bursera*.

$d^{15°}$ 0·875-0·890 ; $\alpha_D -3°$ to $-5°$, less frequently dextrorotatory $+3°$ to $+8°$; saponification value 1-25 ; soluble in 2 vols. of 70 per cent. alcohol.

Mustard Oil, true.—From the seed of *Brassica nigra*, Koch, and *Brassica juncea*, Hooker.

$d^{15°}$ 1·014-1·025 ; $\alpha_D \pm 0°$; boils for the most part between 147° and 153° (760 mm.) ; soluble in every proportion in 90 per cent. alcohol. Allyl isothiocyanate content more than 90 per cent.

Mustard Oil, synthetic —$d^{15°}$ 1·020-1·025 ; $\alpha_D \pm 0°$. Boils chiefly between 150° and 153° (760 mm.). $n_D 20$ 1·527-1·529.

Determination of the Allyl Isothiocyanate in Mustard Oil.—A method for the quantitative determination of sulphur in mustard oil has been devised by J. Gadamer[1] and improved by M. Kuntze.[2] The mustard oil is converted by ammonia into thiosinamine (allyl thiocarbamide), and the latter by an ammoniacal solution of silver nitrate into silver sulphide, allyl cyanamide, and ammonium nitrate, in accordance with the equation :—

$$C_3H_5.NCS + 3NH_3 + 2AgNO_3 = Ag_2S + C_3H_5.NCNH + 2NH_4NO_3.$$
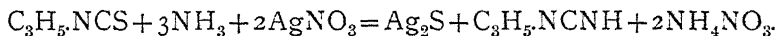
In order that this reaction should proceed smoothly, a large excess of silver nitrate is necessary. If conducted in alcoholic solution, it is also necessary that this should be heated, as otherwise the results are too low. The excess of silver nitrate is titrated back with $N/10$ ammonium thiocyanate solution.

For testing the mustard oil it is first converted into the Spirit of Mustard (*Spiritus Sinapis* of the German Pharmacopœia) by mixing 2 g. of the oil with 98 g. of alcohol (sp. gr. 0·830-0·834).

The determination is carried out as follows :—To 5 c.c. (=4·2 g.) of the spirit, contained in a flask of 100 c.c. capacity, are added 50 c.c. of $N/10$ silver nitrate solution and 10 c.c. of solution of ammonia (sp. gr. 0·960). After closing the flask with a cork, through which a glass tube 1 m. in length is passed, the mixture is heated for an hour on a water-bath in which the water is in active ebullition. It is then cooled to 15°, the flask filled to the 100 c.c. mark with distilled water, and the mixture filtered. In 50 c.c. of the clear filtrate, after the addition of 6 c.c. of

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[1] *Arch. Pharm.*, 1899, **237**, 110, 372 ; *J. Chem. Soc. Abstr.*, 1899, **76**, ii., 712.

[2] *Arch. Pharm.*, 1908, **246**, 58 ; *J. Chem. Soc. Abstr.*, 1908, **94**, ii. 440.

nitric acid (sp. gr. 1·153), the excess of silver nitrate is determined by titration with $N/$10 ammonium thiocyanate solution, ferric ammonium sulphate or ferric sulphate being used as the indicator.

Since 2 mols. of silver nitrate (M.W. = 340) correspond to 1 mol. of allyl mustard oil (M.W. = 99), 1 c.c. $N/$10 silver nitrate solution (= 0·017 g. AgNO₃) is equivalent to 0·00495 g. of allyl mustard oil.

Nutmeg Oil.—Distilled from nutmeg, the kernel of the seed of *Myristica fragrans*, Houttuyn.

$d^{15°}$ 0·870-0·925 ; a_D +7° to +30° ; soluble in 1-3 vols. of 90 per cent. alcohol.

Orange Oil, bitter.—Expressed from the rind of the fruit of the bitter orange, *Citrus Bigaradia*, Risso.

$d^{15°}$ 0·853-0·857 ; a_D +90° to +93° at 20° C. Does not form a clear solution with 90 per cent. alcohol. Residue on evaporation (see under Bergamot Oil, p. 269) 3-5 per cent.

Orange Oil, sweet.—Expressed from the rind of the fruit of the sweet orange, *Citrus Aurantium*, Risso.

d 15° 0·848-0·853 ; a_D +95° 30' to +98° at 20° C. Does not form a clear solution with 90 per cent. alcohol. Residue on evaporation 2-4 per cent.

Orange Flower Oil. *Oil of Neroli.*—A distillate from the flowers of the bitter orange, *Citrus Bigaradia*, Risso.

$d^{15°}$ 0·870-0·880 ; a_D +1° 30' to +8° ; soluble in 1-2 vols. of 80 per cent. alcohol, but on the further addition of the solvent a turbidity usually occurs owing to the separation of a paraffin ; saponification value 24-55.

Palmarosa Oil (also incorrectly termed Indian or Turkish Geranium Oil).—From the herb. of *Cymbopogon Martini*, Stapf.

$d^{15°}$ 0·888-0·900 ; a_D slightly dextro- or lævorotatory +6° to −2° 30' ; soluble in 1·5-3 vols. of 70 per cent. alcohol ; saponification value 14-46 ; saponification value after acetylation not below 225.

Patchouli Oil.—From the leaves of *Pogostemon Patchouli*, Pelletier.

$d^{15°}$ 0·970-0·995 ; a_D −50° to −68° ; soluble in 1 vol. of 90 per cent. alcohol.

Peppermint Oil.—From the herb of *Mentha piperita*, Linné. There are various commercial sorts of this oil, of which the English, American, and Japanese are the most important.

English or Mitcham Peppermint Oil.—$d^{15°}$ 0·900-0·910 ; a_D −22° to −33° ; soluble in 3-5 vols. of 70 per cent. alcohol. Amount of ester menthol (*i.e.* menthol present in the form of ester, calculated as menthyl acetate, $C_{10}H_{19}O . COCH_3$) 4-12 per cent. = saponification value 14-41 ; total menthol (free menthol+menthol ester) 50-63 per cent. = saponification value after acetylation 164-194.

American Peppermint Oil.—$a^{15°}$ 0·900-0·920 ; a_D −18° to −33°.

Some oils only dissolve in $\frac{1}{2}$ vol. and more of 90 per cent. alcohol, whilst others are soluble in 4-5 vols. of 70 per cent. alcohol. Ester menthol 3-10 per cent. (saponification value 10-36), total menthol 50-61 per cent. (saponification value after acetylation 158-188).

Japanese Peppermint Oil.—At the ordinary temperature a normal oil is a semi-solid mass, interspersed with crystals of menthol. The commercial oils are mostly such as have been deprived of a part of the menthol, and which therefore vary exceedingly with respect to density, rotatory power, and menthol content. The differentiation of the individual sorts of peppermint by a physical and chemical examination is very difficult, and impossible in the case of mixtures of different oils.

Rose Oil.—From the flowers of *Rosa damascena*, Miller.

$d^{30°}$ 0.849-0.862; a_D −1° 30′ to −3°. On account of the paraffin hydrocarbons present, the oil does not give a clear solution with 90 per cent. alcohol. Acid value 0.5-3.0; ester value 8-16; total geraniol content (geraniol + citronellol) 66-75 per cent. (see p. 263). Congealing point (*i.e.* the temperature at which the oil, when slowly cooled, begins to separate the stearopten or paraffins) +19° to +23°·5. In order to determine the congealing point of rose oil, 10 c.c. of the oil are brought into a test tube of 15 mm. diameter, and a thermometer then immersed in it so that it can move freely without touching the sides of the glass. After the test tube has been warmed to such an extent that all the stearopten is melted, the contents are slowly cooled until the first crystals appear.

Rosemary Oil, Italian.—From the flowers of *Rosmarinus officinalis*, Linné.

$d^{15°}$ 0.900-0.920; a_D dextrorotatory to +15°; soluble in $\frac{1}{2}$ vol. and more of 90 per cent. alcohol. If from 50 c.c. of the oil, contained in the flask described on p. 262, 5 c.c. are slowly distilled off, the distillate should be dextrorotatory. If it is lævorotatory, this is almost always due to an adulteration with French oil of turpentine. It should, however, be noted that there are also pure natural products of which the first 10 per cent. which passes over is slightly lævo-rotatory. The German tax commissioners no longer give definite directions for the examination of rosemary oil which is to be used for denaturing fatty oils.

Sandalwood Oil.—From the wood of *Santalum album*, Linné.

$d^{15°}$ 0.975-0.983; a_D −15° to −20°; soluble in 5 vols. of 70 per cent. alcohol at 20°, and this solution should not be rendered turbid by the further addition of 70 per cent. alcohol; saponification value 5-20. Santalol content, calculated for $C_{15}H_{24}O$, at least 91 per cent. (for method of determination, see p. 263).

Sassafras Oil.—From the root of *Sassafras officinalis*, Nees.

$d^{15°}$ 1·070-1·082 ; a_D +3° to +4° ; soluble in 1-2 vols. of 95 per cent. alcohol.

Safrol, $C_{10}H_{12}O_2$.—$d^{15°}$ 1·105-1·107; a_D ± 0°; boiling point 233° (760 mm.); n_D 20° 1·536-1·540. Congealing point 11°. Safrol often solidifies with great difficulty, and the crystallisation should therefore be initiated by introducing a crystal of the substance.

Spike Oil.—Distilled from the flowers of *Lavandula Spica*, DC.

$a^{15°}$ 0·905-0·915 ; a_D dextrorotatory to +7°; soluble in 1·5-3 vols. of 70 per cent. alcohol. The best spike oils dissolve in 15-20 vols. of 60 per cent. alcohol. Saponification value 5-20.

Star-anise Oil.—From the fruits of *Illicium anisatum*, Linné.

$d^{15°}$ 0·980-0·990; a_D slightly lævorotatory to −2°, seldom slightly dextrorotatory; soluble in 1·5-2·5 vols. of 90 per cent. alcohol. Congealing point (see p. 260) +15° to +18°.

Thyme Oil.—From the fresh flowering herb of *Thymus vulgaris*, Linné.

$d^{15°}$ 0·900-0·915 ; a_D slightly lævorotatory; phenol content (thymol and carvacrol) 20-30 per cent. (for method of determination see p. 266); soluble in 1-2 vols. of 80 per cent. alcohol.

Thymol, $C_{10}H_{14}O$.—$d^{15°}$ 1·028; crystallised thymol sinks in water, but in a fused state floats upon it. Melting point 50°-51°; boiling point 228°-230° ; readily soluble in alcohol, ether, chloroform, and the aqueous solutions of caustic alkalis, but very slightly soluble (1 : 1100) in pure water.

Turpentine Oil.—Distilled from the turpentine of various species of *Pinus*.

American Turpentine Oil.—$d^{15°}$ 0·865-0·870; a_D dextrorotatory to +15°, very seldom slightly lævorotatory; soluble in 5-7 vols. of 90 per cent. alcohol, old resinified oil being more readily soluble. On distillation 85 per cent. passes over between 155° and 163°.

French Turpentine Oil.—$d^{15°}$ 0·865-0·876; a_D −20° to −40°. The other properties are the same as those of the American oil.

Spanish Turpentine Oil.—This possesses the same constants as the French oil.

Grecian Turpentine Oil.—$a^{15°}$ 0·863-0·870; a_D +36° to +40°. Otherwise the same as the American oil.

Pine-tar Oil (Ger. *Kienöl*) is a product of the dry distillation of coniferous roots, and may be recognised by its disagreeable, empyreumatic odour. $d^{15°}$ 0·862-0·875 ; a_D +14° to +24.° It boils between 160° and 180°.

Turpentine oil has been much adulterated in recent years, chiefly with fractional products from petroleum (benzine, etc.), rosin essence, carbon tetrachloride, pine-tar oil, and many other substances. The detection, and especially the quantitative determination of these

additions, is often difficult ; for a critical consideration of the respective methods reference should be made to the work of J. Marcusson and H. Herzfeld.[1]

An addition of benzine may be recognised by a lowering of the specific-gravity, since that of pure turpentine oil is between 0·865 and 0·875, whilst the benzine fractions commonly used to adulterate it, which boil from 100°-180°, have a density between 0·73 and 0·80. The indices of refraction are also different, that of turpentine oil being 1·471-1·4735 and that of benzine 1·419-1·450. According to Herzfeld the addition of benzine may also be recognised by fractional distillation. In the case of a pure oil the refraction indices of the individual fractions will differ but slightly from each other, whereas the portions containing benzine will exhibit great differences.

The quantitative determination of petroleum in turpentine oil is carried out according to W. M. Burton[2] as follows :—300 c.c. of fuming nitric acid are allowed to drop slowly from a dropping funnel into 100 c.c. of the adulterated oil, contained in a capacious flask provided with a reflux condenser, the mixture being kept well cooled. The product of the reaction is then washed with hot water, and the residual petroleum weighed.

For this method of determination H. Herzfeld[3] has constructed a small apparatus (Fig. 50), which renders it possible directly to read off the amount of mineral oil which has not been attacked by the nitric acid.

Herzfeld[4] subsequently recommended the use of fuming sulphuric acid in the place of nitric acid. 10 c.c. of the turpentine oil to be tested are allowed to drop slowly, with moderate cooling, into 40 c.c. of concentrated sulphuric acid. After ten to twelve hours from 8-9 per cent. of the turpentine oil used will separate. The lower dark brown layer is then drawn off, and the residual oil again shaken with 3-4 c.c. of fuming sulphuric acid. After standing for several hours only 0·1-0·2 c.c. of oil will then separate, whereas if a mineral oil be present, the volume will be correspondingly greater.

FIG. 50.

According to Marcusson it is better to treat the sample of oil at − 10° with fuming nitric acid ; but opinion is still divided respecting the relative merits of the nitric acid and sulphuric acid methods. The
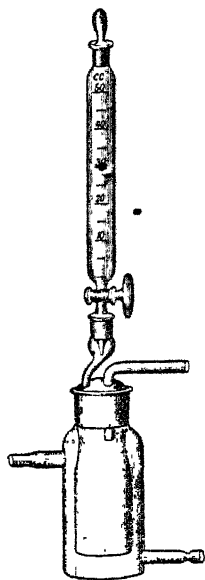
[1] *Chem. Zeit.*, 1909, **33**, 966, 985, 1081 ; 1910, **34**, 285 ; 1912, **36**, 413, 421. *Cf.* also *J. Soc. Chem. Ind.*, 1909, **28**, 1096.

[2] *Amer. Chem. J.*, 1890, **12**, 102 ; *J. Soc. Chem. Ind.*, 1890, **9**, 557.

[3] *Chem. Zentr.*, 1903, **1**, 258.   [4] *Ibid.*, 1904, **1**, 548.

results vary greatly, especially for the reason that the different sorts of petroleum (from America, Russia, Galicia, Sumatra, and Borneo) show a very different behaviour towards the two acids.

Pine-tar oil may be recognised by the fact that a fragment of potassium hydroxide, when brought into the liquid, will soon become coated with a yellowish-brown layer. In the case of pure turpentine oil, considerable time will elapse before the formation of such a layer occurs. Old, resinified oils should be distilled before the application of this test. Pine-tar oil, in amounts of not less than 10 per cent., may be detected by the yellowish-green coloration produced by sulphurous acid (Herzfeld's reaction).[1]

Rosin essence may be recognised, apart from the low temperature at which the liquid begins to boil, by Grimaldi's reaction, which depends upon the collection of fractions of oil, in amounts of 3 c.c. each, up to a temperature of 170°, and the green coloration which they yield with a fragment of tin and hydrochloric acid.

Carbon tetrachloride, which, on account of its higher density, is used to conceal an adulteration with benzine, may easily be detected by Beilstein's copper test, or by the separation of potassium chloride when boiled with an alcoholic solution of potassium hydroxide, as also by fractional distillation. For its quantitative determination when mixed with turpentine oil and benzine, the chlorine content of the mixture is determined according to the method of Carius. Pure carbon tetrachloride contains 92·2 per cent. of chlorine.

[1] *Cf.* also Wolff, *Chem. Zeit. Rep.*, 1912, **36**, 64 ; *J. Soc. Chem. Ind.*, 1912, **31**, 692 ; and Piest, *Chem. Zeit.*, 1912, **36**, 198 ; *J. Soc. Chem. Ind.*, 1912, **31**, 239.

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TARTARIC ACID

By W. KLAPPROTH, Dr Ing., Chemist to Messrs C. H. Boehringer, Nieder-Ingelheim,
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THE residues from the manufacture of wine are the raw materials for
the tartaric acid industry. From these residues are manufactured
tartaric acid, cream.of tartar, and several other salts of tartaric acid,
such as Rochelle salt, normal ("neutral") potassium tartrate, tartar
emetic, and tartrate of iron.

These raw materials may be classified as follows :—*Lees, tartars*
(especially the so-called "*alambic*" and "*vinaccia*" tartars) and "*tartrate
of lime.*" They are obtained by drying, or by crude processes of
crystallisation, or precipitation, from the residues obtained in the manu-
facture of wine. The tartaric acid is present in these materials in the
form of potassium hydrogen tartrate (bitartrate), or as normal calcium
tartrate, or as a mixture of both these substances; the proportions are
very variable.

Wine-lees, the sediment that settles out from the completely
fermented must, is the most important raw material. In the moist
condition, as obtained by pressing out the new wine from this sediment,
lees form a sticky, clay-like mass, with an odour of wine, and having a
dirty yellow to dark red colour. The lees are dried as quickly and
rapidly as possible, in order to avoid the decomposition of the tartaric
acid by the growth of moulds or bacteria, and are usually put on the
market in this form as *dried lees*. They consist of yellowish to dark red,
irregularly shaped lumps, with an average size about that of a walnut.
The content of tartaric acid is usually between 15-30 per cent., but is
sometimes as high as 40 per cent., although lees of the latter grade are
seldom or never worked in this country. The tartaric acid is present
as acid potassium tartrate and calcium tartrate in variable proportions.
The rest of the material is made up of the dried yeast-cells, small
amounts of inorganic salts, and "impurities" which arise from the grape-
juice, or from the materials used in treating the wine (grape-skins,
stalks, pips, clay, sulphur, sand, and gypsum). Lees are differentiated
according to the place of origin as Italian, Spanish, French, Austrian,
and Levantine. The last-named includes Dalmatic, Greek, Turkish,
and South Russian lees. Lees show very marked differences, especially

as regards working, according to their place of origin; analyses have been published by Warington, Rasch, and Ciapetti.[1]

The name of "*Tartars*" comprises the raw materials which contain more than 40 per cent. of tartaric acid. A distinction is to be made between cask-tartars, obtained by the chipping of the scale from wine casks, and the tartars obtained by boiling out with water the lees and *marc* or *vinacce* from the manufacture of wine, and subjecting the liquors to crystallisation; tartars obtained in this latter way form the higher-grade tartars, such as *Vinaccia tartar*. The best half-refined tartar, known as *St. Antimo tartar*, serves for the manufacture of cream of tartar, Rochelle salt, and other tartaric acid salts.

Limo, Sablon, and *Tartrate of Lime* are raw materials obtained by the precipitation of tartaric acid in tartar works or wine-distilleries.

I. RAW MATERIALS.

Owing to the relatively high value of raw materials for the manufacture of tartaric acid and the fact that they are frequently very far from uniform in character, the sampling must be carried out with very special care. For this purpose a portion of the material is taken from each cask or sack, and in general the procedure described in Vol. I., Part I., pp. 12-14 is followed. The material is first coarsely ground in the factory mill during the sampling, and then, before analysis, again finely ground in the laboratory in an ordinary small hand-mill (coffee mill) kept solely for this purpose.

In judging the raw material, both the total percentage of tartaric acid and the percentage of tartaric acid present as bitartrate are of importance; the former is necessary in all branches of the tartaric acid industry, whilst the latter is essential in the manufacture of cream of tartar and of salts of tartaric acid. The analytical results for the so-called "Total acid" are given as the percentage of tartaric acid in the raw material; the "Bitartrate" is expressed either as the percentage of potassium hydrogen tartrate, or as its equivalent in tartaric acid. In England the latter method has been generally used in the analysis of lees and tartars. It is not a general practice to return the percentage of moisture present in the sample, although by neglecting this, not only can differences of analysis arise, but also an essential factor for judging the raw material is left out of account. Insufficiently dried samples often lose several per cent. of tartaric acid in a few weeks, owing to the development of moulds and bacteria; even apparently well-dried samples of lees, when kept in carefully sealed glass bottles, have been shown to lose from 1-3 per cent. of their tartaric acid in five years. Moreover, slimy substances are

[1] See *Literature*, p. 295.

produced in insufficiently dried material owing to the growth of moulds, and these give trouble in subsequent factory working. It is therefore desirable to determine the percentage of moisture obtained by drying the sample at 100°.

In estimating either the bitartrate or the total tartaric acid, the tartaric acid is precipitated in the form of the acid potassium salt, which is then determined by titration. For the titration, $N/10$, $N/5$, $N/2$, or $N/1$ potassium hydroxide is used, which must be free from carbon dioxide; it is standardised by titration with specially recrystallised potassium hydrogen tartrate (dried at 100°) under exactly the same conditions of concentration as are used in the actual determination. As indicator, sensitive reddish-violet litmus paper is used exclusively; the same paper must be used in standardising as in the actual estimation. The test is made by "spotting."

The molec. wt. of tartaric acid = 150.

    „   „   potassium hydrogen tartrate = 188.

1. The Estimation of Acid Potassium Tartrate (Bitartrate).

An approximate estimation of bitartrate is effected by simple titration. With lees of average quality containing from 20-30 per cent. of tartaric acid, the results obtained in this way are from 3-5 per cent. higher than the true bitartrate values, owing to the presence of acid salts and organic substances of acid character; with unadulterated tartars the difference is smaller. This method does not accordingly indicate the adulteration of the raw material with acid substances such as alum.

Approximate results are also obtained by several other methods which were formerly in use, such as the "Ignition method" and the "Méthode à la casserole." In the former method, the material was burnt, the ash extracted with water and the dissolved potassium carbonate estimated. In the French "casserole test," the sample was extracted with boiling water and the crystals which separated on cooling weighed. The methods described in detail by P. Carles[1] are not applicable, because when certain impurities are present, either by accident or design, quite incorrect results are obtained.

The method of Philips & Co.[2] consisted in exactly neutralising the bitartrate with potassium hydroxide and reprecipitating it from the filtered solution by acetic acid and alcohol. When other calcium salts are present, such as gypsum, the results obtained are too high.

F. Klein[3] boils the sample with water, evaporates the filtered solution to a small volume, and precipitates the bitartrate by adding potassium chloride. The precipitate is filtered off, washed with a 10 per

[1] *Les Dérivés Tartriques*, 1903 ; *Z. angew. Chem.*, 1898, **11**, 183.

[2] *Z. anal. Chem.*, 1890, **29**, 577.   [3] *Ibid.*, 1885, **24**, 379.

cent. solution of potassium chloride which has previously been saturated with the bitartrate, and then titrated. This method, which is based on Warington's process for the estimation of the total tartaric acid, is not now in general use, although it gives good results; it has been much recommended by Fabre.[1]

The most-used commercial method, the so-called "Oulman's method," is described by Stiefel[2] as follows:—3.76 g. of the finely powdered tartar is placed in a litre flask, 750 c.c. of water added, the latter heated to boiling and kept in ebullition for not more than five minutes. The flask is then filled to the mark with distilled water and allowed to cool. After cooling, the volume is adjusted to the exact litre and the solution filtered through a dry filter. Of this solution, 500 c.c. are evaporated to dryness on the water-bath in a porcelain dish, the residue moistened with 5 c.c. of water, and after cooling, mixed with 100 c.c. of 95 per cent. alcohol. After standing for thirty minutes the alcohol is decanted through a dry filter paper, allowed to drain thoroughly, and any potassium bitartrate which has passed on to the filter paper is washed back into the dish with boiling water. The solution is then made up to about 100 c.c. and titrated whilst hot with $N/5$ potassium hydroxide. To the number of cubic centimetres of alkali used 0.2 c.c. is added to correct for the loss of bitartrate in the alcohol mother liquors.

All methods for estimating bitartrate are scientifically not quite accurate, as changes may occur in boiling out the samples; for this reason, too prolonged boiling should be avoided.

2. The Estimation of the Total Tartaric Acid.

The older methods of Scribani, Scheurer-Kestner, and Oliveri, based on the precipitation and weighing of calcium tartrate, have been abandoned on account of their inaccuracy.

The first scientifically sound method was that of R. Warington,[3] the principle of which is as follows:—The calcium present was precipitated as oxalate by means of neutral potassium oxalate, the mass neutralised with potassium hydroxide, the whole filtered, and the tartaric acid in solution separated by means of citric acid in presence of potassium chloride. This method, which was improved by Grosjean[4] and A. Bornträger,[5] although in use commercially for many years, and until recently exclusively in this country, has been largely abandoned owing to its tediousness and also to the fact that it gives decidedly high results in presence of impurities such as phosphates.

The method which is now in general use for the estimation of

[1] *Chem. Zeit. Rep.*, 1899, **23**, 4.　　　[2] *Das Raffineren des Weinsteins*, 1894.
[3] *J. Chem. Soc.*, 1875, **27**, 925.　　　[4] *Ibid.*, 1879, **35**, 341; 1883, **43**, 331.
[5] *Z. anal. Chem.*, 1886, **25**, 327; 1887, **26**, 699.

the total tartaric acid is the "Goldenberg Method, 1898," and its modification known as the "Goldenberg Method, 1907."

These methods are based in principle upon a process, apparently due to Jules, and described in detail by the firm of Goldenberg, Géromont & Co., which was adopted in the industry under the name "Original Goldenberg Method."[1] This method was carried out as follows:—The substance was boiled with an excess of potassium carbonate, whereby the calcium was precipitated as carbonate, and the tartaric acid converted into the normal potassium salt; the solution was then filtered and an aliquot portion of the filtrate precipitated by acetic acid and alcohol, the precipitated bitartrate being washed with alcohol and titrated. This method is subject to the following errors:— The potassium hydrogen tartrate is not quite insoluble in the mixture of dilute alcohol and acetic acid; on the other hand, especially in the case of wine-lees, other acid substances (pectic material) are precipitated and finally titrated as bitartrate. The results were, therefore, uniformly considerably higher than the true tartaric acid content, and depended on the excess of potassium carbonate employed; further, the solutions of bitartrate finally titrated were always highly coloured, so that the results obtained by different analysts often differed widely, sometimes by several per cent.

These difficulties are avoided in the "Hydrochloric Acid Method," also due to the firm of Goldenberg, Géromont & Co. The first form of the method published in 1888[2] was defined in greater detail in 1898.[3]

The "Goldenberg Method, 1898."

This method is carried out as follows:—6 g. of finely ground and powdered lees are stirred into a uniform mass with 9 c.c. of dilute hydrochloric acid (sp. gr. 1·1), and allowed to stand during one hour at the ordinary temperature, with frequent stirring. The mixture is then diluted with an equal volume of water and again left for an hour, stirring from time to time. The mass is now washed into a 100 c.c. measuring flask, and the volume made up to the mark. After shaking well, the solution is filtered through a dry filter paper into a dry vessel; 50 c.c. of the filtrate are then measured into a beaker which is kept covered with a clock-glass, and carefully boiled with 18 c.c. of a potassium carbonate solution (10 c.c. = 2 grm. K_2CO_3) for ten minutes until the calcium carbonate is separated in a granular form. After washing the clock-glass with water, the contents of the beaker are filtered and the beaker washed with boiling water until the washings are neutral; the calcium carbonate on the filter paper is also thoroughly washed out with boiling water, the alkaline liquid being

[1] Z. anal. Chem., 1883, 22, 270.   [2] Chem. Zeit., 1888, 12, 390

[3] Z. anal. Chem., 1898, 37, 312, 383.

finally transferred to a porcelain dish. The liquid is then evaporated to about 15 c.c, and, after covering the dish with a clock-glass, carefully mixed while hot with 3 c.c. of glacial acetic acid. After stirring for five minutes the analysis may be completed, or, if necessary, left for some time, even to the next day if desired. This long standing, however, should be avoided in the case of low-grade lees, as a slimy precipitate may separate from which it is difficult subsequently to wash out the acetic acid completely. If, for any reason, the analysis must be interrupted at any other point, this is best done after measuring out the 50 c.c. of the hydrochloric acid solution.

After stirring with acetic acid, 100 c.c. of 94-96 per cent. alcohol is added, rinsing the clock-glass therewith as it is run in; the mixture is then stirred continuously during another five minutes, until the precipitate, which first separates as curds, has become finely granular-crystalline. The precipitate of bitartrate is now immediately transferred to a conical suction-filter in the following way :—The precipitate is first allowed to settle in the dish in the ordinary manner, and the alcohol decanted off through the filter paper; the precipitate is then washed on to the paper and the dish washed out with alcohol until there is no further acid reaction. The precipitate on the filter is also washed with alcohol until 30 c.c. of the alcoholic filtrate mixed with phenolphthalein shows an alkaline reaction after adding 2-3 drops of $N/5$ potassium hydroxide; this quantity of alkali is that required to overcome the slight acidity of the alcohol employed. Finally, the precipitate, together with the filter paper, is transferred to a beaker, the bitartrate adhering to the porcelain dish and clock-glass being also washed in by means of boiling water, so that a total volume of from 100-120 c.c. of liquid is obtained. This is titrated with $N/2$ potassium hydroxide; $N/1$ potassium hydroxide can be used if a burette of 10 c.c. capacity, graduated in $\frac{1}{50}$ c.c., be employed, so that accurate readings to within $\frac{1}{100}$ c.c. can be obtained. To recognise the end point *sensitive* litmus paper, with a reddish-violet colour, is used. The alkali used must be standardised with chemically pure potassium hydrogen tartrate, using the same litmus paper and about the same concentration of solution as in the actual analyses. The calculation is corrected in the following way for the volume of lees-residue remaining undissolved by hydrochloric acid in the first instance :—With a tartaric acid content of 20 per cent., a deduction of 0·7 per cent. is made; and the apparent value $(20+n)$ per cent. is counted as $(20+n)$ per cent. $-$ $(0·7+0·02\,n)$ per cent. tartaric acid.

In analysing tartars and tartrate of lime, 3 g. of substance is employed, which is digested with 9 c.c. of hydrochloric acid, diluted to 100·5 c.c., and 50 c.c. of the filtrate is used for the analysis, as above. In these cases the above correction is avoided.

In the case of normal raw materials, not too much contaminated by factory impurities, this method gives results corresponding with the actual tartaric acid content. High results due to adulterants are not possible. Experience, however, has shown that certain points were not sufficiently defined, considerable differences being found in the results of different analysts, especially in the case of lees rich in calcium tartrate. The manner in which the potassium carbonate was added to the hydrochloric acid solution—whether rapidly or slowly—and the time of heating, etc., were found to affect the result. These differences are not so pronounced when, conversely, the hydrochloric acid solution is added slowly to the potassium carbonate. In order to obviate them the exact details of procedure to be adopted were discussed at the International Congresses of Applied Chemistry held at Rome in 1906, and at London in 1909, and the following modification was agreed upon, which is, in the main, that worked out by Messrs Ogston and Moore.[1] This modification is known as :—

The " Goldenberg Method, 1907."

This revised form of the Goldenberg method is carried out as follows :—6 g. of the sample if it contains more than 45 per cent. of tartaric acid, or 12 g. if it contains less than 45 per cent., is stirred continuously during ten minutes with 18 c.c. of hydrochloric acid of sp. gr. 1·10. The mass is then washed into a 200 c.c. measuring flask, made up to the mark with distilled water, and, after shaking well, the solution is filtered through a dry, fluted filter into a dry beaker. 100 c.c. of the filtrate is then measured out by a pipette (the volume of which agrees exactly with the graduated flask—"standard" measuring vessels should be used by preference) and added to 10 c.c. of a solution of potassium carbonate containing 66 g. of the anhydrous salt per 100 c.c. (sp. gr. 1·490). The solution of the potassium carbonate is placed in a beaker of 300 c.c. capacity, which should be covered with a clock-glass during the addition of the 100 c.c. of acid solution. After mixing, the solution is boiled gently for twenty minutes, until the calcium carbonate has separated in a crystalline form. The liquid is then washed into a 200 c.c. measuring flask, cooled, made up to the mark, and filtered through a dry, fluted filter paper.

100 c.c. of the filtrate is then evaporated, either in a porcelain dish[2] on the water-bath, or in a beaker of Jena glass, on a hot plate, until the volume is about 15 c.c. Whilst the solution is still hot 3·5 c.c. of glacial acetic acid is added gradually, and with constant stirring, and

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[1] *Z. anal. Chem.*, 1908, **47**, 57. *Report of International Committee on Analysis*, 7th International Congress of Applied Chemistry, London, 1909.

[2] Porcelain basins having a blue ring on the inside to show the volume of 15 c.c., can be obtained from B. W. Haldenwanger, Charlottenburg.

the stirring continued for five minutes afterwards. After standing for
ten minutes longer, 100 c.c. of 95 per cent. alcohol is added and the
mixture again stirred during five minutes. After a further ten minutes'
interval, the precipitate of bitartrate is filtered by the aid of a vacuum
pump; for this filtration a perforated disc of lead or porcelain is used,
with a filter paper cut slightly larger than the disc. Asbestos pulp can
also be used. The precipitate is then washed with alcohol until the
washings cease to give an acid reaction, the washing being continued
until 30 c.c. of the filtrate, mixed with phenolphthalein, require exactly
the same volume of $N/5$ alkali to produce redness as 30 c.c. of the
alcohol itself. The filter with the precipitate is washed into a porcelain
dish with about 200 c.c. of boiling water, and then titrated with $N/5$
potassium (or sodium) hydroxide solution, using sensitive litmus paper[1]
as indicator (spot test).

The alkali must be standardised with chemically pure potassium
hydrogen tartrate (dried at 100°) using the same litmus paper and
approximately the same concentration of solution.

As the volume of the insoluble constituents of the raw material has
not been taken into consideration the following corrections are
necessary :—It has been agreed to deduct 0·8 per cent. for raw material
yielding less than 45 per cent. of total tartaric acid, 0·3 per cent. for
raw material with 45-60 per cent., and 0·2 per cent. for material with
60-70 per cent. No deduction is made in the case of samples with
more than 70 per cent. of acid.

The " 1907 Method" gives slightly higher results than the " 1898
Method," by an amount which varies between 0·2 and 0·7 per cent.
In consequence a slightly lower valuation of the raw material is
found with the new method. Both methods are in use, some dealers
preferring to use the one, some the other method. As compared with
the older Warington method, the Goldenberg 1907 method gives
results from 1·5-1·7 units lower; that is, a difference in the case of
lees of about 6 per cent. and in the case of tartars of 3 per cent. on the
tartaric acid present.

Several other methods have been proposed for estimating tartaric
acid, but none of these has been generally adopted. It will be
sufficient therefore to give the references.

J. Mosczenski.[2]—Extraction of the material with sulphuric acid, and
direct precipitation with potassium acetate.

K. Ulsch.[3]—Action of the material on platinised iron powder, and
measurement of the hydrogen liberated.

H. Ley.[4]—Precipitation and weighing as zinc tartrate.

[1] The most suitable sensitive litmus paper is that obtainable from E. Merck, Darmstadt, or
E. Dieterich, Helfenberg.   [2] *Z. anal. Chem.*, 1900, 39, 57.
    [3] *Z. anal. Chem.*, 1901, 40, 614.   [4] *Pharm. Zeit.*, 1904, p. 149.

P. Carles.[1]—Precipitation of a hydrochloric acid extract with calcium acetate, and weighing of the separated crystals of calcium tartrate.

The following are references to more recent methods:—

A. C. Chapman and P. Whitteridge, *Analyst*, 1907, **32**, 163·

P. Pozzi-Escot, *Comptes rend.*, 1908, **146**, 1031.

A. Kling, *Comptes rend.*, 1910, **150**, 616.

C. Béis, *Bull. Soc. Chim.*, 1910, **7**, 697.

3. Other Estimations.

The adulteration of the raw material employed in the manufacture of tartaric acid, for example with alum, was formerly practised when samples were examined merely by simple. titration; since the introduction of the Warington and Goldenberg methods, such adulteration is no longer met with. The addition of alum would in fact cause an apparent loss of real tartaric acid in the Goldenberg method.

When the final mother liquors ("Old Liquors") of the tartaric acid industry, in which impurities such as alumina, iron, and phosphoric acid have accumulated, are precipitated in the form of calcium tartrate, the harmful impurities tend to separate also. The working up of these old liquors is attended with difficulties. It, therefore, may happen that a parcel of raw material is contaminated with such a product. Such adulteration, which can in many cases be detected by smell, is also recognised by estimating the ratio of phosphoric acid, alumina, and iron to the total tartaric acid present (*Impurity Ratio*). For this determination a portion of the sample is ignited; if much calcium tartrate be present, it is advisable to moisten the material with a concentrated sugar solution in order to avoid loss. The ash is extracted with hydrochloric acid, and in the acid extract phosphoric acid, alumina, and ferric oxide are estimated; it is generally sufficient to precipitate the three substances together by adding ammonia, and to weigh the whole after ignition. The amount found is calculated as a percentage of the total tartaric acid present.

To estimate the proportion of iron the ignited material is dissolved by boiling with dilute sulphuric acid, cooled, reduced with iron-free zinc, and the solution titrated with $N/10$ potassium permanganate.

The "Impurity Ratio" determined in this way is, in general, for tartars, less than 1, for lees from 1-2, and only seldom in the latter case reaches 5-6; in impure factory products the ratio reaches 10-20.

By slow or unsatisfactory drying, slimy substances may be formed in lees, owing to the growth of moulds or bacteria which render the subsequent working up of the products very inconvenient. It is,

[1] *Les Dérivés Tartriques*, 1903, p. 105.

therefore, necessary to ascertain in many cases whether a material
contains an undesirable quantity of such fermentation organisms. This
is done as follows, according to the method given by H. Rasch[1]:—40 g.
of lees are mixed with 50 c.c. of 10 per cent. calcium chloride solution
in a beaker of 400 c.c. capacity, and exactly neutralised with milk of
lime in the cold. The beaker is filled up with water, and the mixture
allowed to stand for twenty-four hours at a temperature of 35°. With
good, well-dried lees no visible fermentation should begin during this
interval; at most, a few bubbles of carbon dioxide should be evolved.

The auxiliary materials of the industry, such as sulphuric acid, lime,
chalk in the case of tartaric acid, sodium and potassium carbonates
in the manufacture of tartaric acid salts, must naturally be as free as
possible from alumina, iron, and phosphoric acid. A small amount of
magnesia in the lime or chalk is not prejudicial in the case of tartaric
acid (as it is in the case of citric acid), because magnesium tartrate is
not very sparingly soluble.

II. Control of Working Conditions.

The impurities which accumulate in the works liquors, which consist
mainly of phosphoric acid, alumina, and iron, are of importance as
regards the estimation of the contained tartaric acid. It has been
shown by Lampert[2] that if litmus be used as the indicator in the
titration of the tartaric acid a certain amount, which is recoverable in
the actual working, escapes estimation. Rasch[3] has therefore recom-
mended the use of phenolphthalein in dealing with works liquors, with
which fairly accurate results can be obtained even though the end-
points are by no means sharp in the case of the cruder liquors.

In the laboratory of Messrs C. H. Boehringer, it is considered
preferable first to remove the iron, the principal impurity, by the
following method:—50 c.c. of the liquor are measured into a beaker
and titrated with a standard solution of potassium ferrocyanide, using
copper sulphate as outside indicator in the usual way, until a slight
brown coloration is shown. The number of cubic centimetres of ferro-
cyanide used gives a measure of the iron present. 50 c.c. of the
original liquor are then measured into a 100 c.c. flask, mixed with the
volume of potassium ferrocyanide found in the previous experiment to
be necessary, made up to the 100 c.c., filtered, and the tartaric acid
estimated in a measured volume of the filtrate. The estimation of the
iron in the works liquors is a useful means of controlling the purity of
these liquors, as the other impurities stand in a nearly constant ratio to
the content of iron.

[1] *Fabrikation der Weinsäure*, p. 44.
[2] *Chem. Zeit.*, 1890, **14**, 903 ; *cf.* also Ordonneau, *Bull. Soc. Chim.*, 1910, **7**, 1034.
[3] *Fabrikation der Weinsäure*, p. 22.

The determinations are carried out as follows :—

Calcium Tartrate.—6 g. of substance are boiled with 10 c.c. of potassium carbonate solution (500 g. per litre) and about 150 c.c. of water for ten minutes, the solution made up to 200 c.c. in a measuring flask, and filtered. 50 c.c. of the filtrate are evaporated to about 15 c.c. and precipitated with 3 c.c. of glacial acetic acid and 100 c.c. of alcohol. The washed precipitate is then titrated with $N/10$ potassium hydroxide to obtain the percentage of tartaric acid, using phenolphthalein as indicator.

Tartaric Acid Liquors.—20 c.c. of the weak liquor (or 10 c.c. of concentrated liquors), freed from iron, are boiled with 40 c.c. of potassium carbonate solution of the above concentration, the solution made up to 200 c.c. and filtered; 10 c.c. of the filtrate are then precipitated hot with 3 c.c. of glacial acetic acid and 100 c.c. of alcohol. The number of cubic centimetres of $N/10$ alkali used in the titration, multiplied by 30, gives grams tartaric acid per litre. Phenolphthalein is used as the indicator.

Old Liquors.—20 c.c. of the old liquor, freed from iron, are boiled with 60 c.c. of potassium carbonate solution, made up to 200 c.c., and filtered. Of the filtrate, 20 c.c. are precipitated with 5 c.c. of glacial acetic acid and 100 c.c. of alcohol. The number of cubic centimetres of $N/10$ alkali used in the titration, multiplied by 15, gives the grams of tartaric acid per litre.

Waste Products—Lees Residue and Gypsum.—300 g. of the sample are heated to boiling in a porcelain dish with 25 c.c. of concentrated hydrochloric acid and 500 c.c. of water, stirring well. A part of the liquid is filtered, and 50 c.c., without evaporation, are precipitated with 3 c.c. of glacial acetic acid and 130 c.c. of alcohol Each 5 c.c. of $N/10$ alkali used in titration corresponds with approximately 0·1 per cent. of tartaric acid in the residue.

Washings or "Runnings." (obtained from the precipitation of calcium tartrate).—200 c.c. of the runnings are evaporated to about 50 c.c., boiled for several minutes with 10 c.c. of potassium carbonate solution, and made up to 100 c.c.; 60 c.c. of the filtrate are then mixed in a measuring cylinder with 10 c.c. of hydrochloric acid of sp. gr. 1·10, and made up with alcohol to a total volume of 180 c.c. The mixture is shaken and filtered immediately, and, without delay, to 150 c.c. of the filtrate is added successively 10 c.c. of potassium carbonate solution (500 g. per litre), 5 c.c. of glacial acetic acid and 100 c.c. of alcohol. The mixture is well stirred, left till the following day, and the precipitate filtered off, washed, and titrated. 10 c.c. of $N/10$ potassium hydroxide correspond with 1·50 g. of tartaric acid per litre. Phenolphthalein is used as the indicator in the titration.

Free Sulphuric Acid in Tartaric Acid Liquors.—20 c.c. of the

liquor are made up to 200 c.c. with alcohol in a measuring flask, left to settle overnight, and filtered; from 100 c.c. of the filtrate the alcohol is completely evaporated on the water-bath, the residue diluted with water, and the sulphuric acid precipitated by barium chloride, and the precipitate collected and weighed as usual.

For the approximate determination of the sulphuric acid it is sufficient to titrate 10 c.c. of the alcoholic solution with $N/5$ barium chloride solution until it ceases to produce a precipitate.

Harmful Impurities ("Impurity Ratio").—Alumina, iron, and phosphoric acid are determined in the same manner as in raw materials (p. 289) on the ash obtained from a known volume of the liquor (20-100 c.c. according to the grade).

The proportion of the ash which is soluble in water is often a useful guide in investigating works liquors, as well as the proportion of potassium carbonate present in this soluble extract. To estimate the potassium carbonate in the ash the quickest and best method is to add from 10-20 c.c. of 5 per cent. barium hydroxide solution to the ash, evaporate to dryness, ignite well, and then extract and filter. To the filtrate (and washings) 5 c.c of perchloric acid (sp. gr. 1·12) are added, and the liquid is evaporated until fumes of perchloric acid are given off strongly. The residue is taken up with 95-96 per cent. alcohol, the precipitate of potassium perchlorate collected on a Gooch crucible or Soxhlet tube, washed first with alcohol containing 0·2 per cent. of perchloric acid, finally with a little pure 95 per cent. alcohol, and weighed.[1] (W. A. D.)

III. Finished Products.

Tartaric Acid.—Dextrorotatory tartaric acid is the only form made commercially. It is used as a mordant in dyeing and as a resist and discharge in printing; also in medicine and photography and on a large scale in the manufacture of baking-powders, effervescent salines, fruit preserves, aerated waters, bon-bons, etc. The acid must be colourless, without smell, and, when crystalline, must consist of large, well-formed transparent crystals. A large quantity of tartaric acid, however, is used in the form of "smalls," that is, consisting of small crystals. Tartaric acid powder must not cake together and should not contain traces of free sulphuric acid, although a trace of sulphate (calcium sulphate) is not prejudicial. Larger quantities of calcium sulphate, however, tend to make tartaric acid hygroscopic; it is generally supposed that this is due to the action of tartaric acid on the sulphate giving rise to free sulphuric acid.

Ash.—The limit for ash in tartaric acid crystal or powder used for

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[1] *Cf.* Section on "Potassium Salts," Vol. I., Part II.; p. 530, and W. A. Davis, *J. Agric. Sci.,* 1912, 5, 56.

pharmaceutical purposes in Great Britain in past years has been 0·05 per cent. The Committee of Reference to the Pharmacopœia Committee (1908) has, however, recommended that this limit should be raised to 0·1 per cent., as there is difficulty in obtaining tartaric acid with ash below 0·05 per cent.

Arsenic is tested for by the following method recommended by the Royal Commission on arsenical poisoning (1903). From 1-5 g. of tartaric acid is used, with arsenic-free zinc and hydrochloric acid. The limit of arsenic adopted is $\frac{1}{100}$ gr. per lb. (1·4 parts As_2O_3 per million, or 0·00014 per cent.). There is no difficulty in obtaining tartaric acid in which arsenic falls considerably below this figure.[1]

Lead.—The limit of lead generally adopted in commerce in this country is 20 parts per million (0·002 per cent.), as recommended by M'Fadden.[2] Many methods have been suggested for making the test, of which the following are probably the most reliable.

Method I.—Based on C. A. Hill's method,[3] which is, like the following one, a modification of Warington's original colorimetric method.[4]

A standard lead solution is prepared containing 5 parts of lead per million, by dissolving pure metallic lead in a minimum quantity of nitric acid (equal parts of concentrated acid and water) and suitably diluting; it is best to prepare a standard stock solution of lead, containing say 1 g. of lead per litre, and then, when required, to dilute this for use to the above concentration. The standard solution may also be prepared from pure lead nitrate or from crystalline lead acetate.

For the test, 7 g. of the sample are weighed out, and a separate portion of 2 g. for the colorimetric comparison. Each portion is dissolved in about 10-15 c.c. of water, and to the 2 g. portion is added as many cubic centimetres of the standard lead solution as there are suspected to be parts per million of lead in the tartaric acid tested. Thus to compare with 15 parts of lead per million, 15 c.c. of the standard lead solution are used. To each solution is then added 1-2 c.c. of 10 per cent. potassium cyanide solution and 13 c.c. of ammonia of sp. gr. 0·880, and the solutions are boiled for half a minute or longer so as to get both colourless if possible. They are next poured into two 50 c.c. Nessler cylinders of clear white glass and diluted to an equal volume (50 c.c.), any difference of colour being corrected if necessary by the addition of a drop or two of a very dilute solution of caramel. To each solution is then added 1-2 drops of a freshly prepared colourless ammonium sulphide solution (obtained by saturating ammonia (sp. gr. 0·880), diluted with an equal volume of water, with hydrogen sulphide gas, carefully washed by passing through water).

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[1] *Cf.* A. W. M'Fadden, Local Government Board Report, Inspector of Foods, No. 2, 1907.

[2] *Cf.* Tatlock and Thomson, *Analyst*, 1908, 33, 173 ; T. F. Harvey and J. M. Wilkie, *Chem. and Drug.*, 1909, 75, 92.

[3] *Chem. and Drug.*, 1905, 66, 388. [4] *J. Soc. Chem. Ind.*, 1893, 12, 97.

The colour of the two solutions is compared by examining them, placed on a sheet of white paper, in a good light.

Generally it is sufficient to make sure that the quantity of lead present is less than 20 parts per million, but if it is necessary to ascertain the exact quantity, comparisons are made with suitable proportions of lead (5, 10, 15, etc. c.c. of the dilute standard lead solution).

Method II.—J. M. Wilkie's Method.[1]—7 g. of the sample are taken for the test, and 2 g. for the colorimetric comparison, to which the standard lead solution is added. Each is dissolved in about 35 c.c. of hot water, allowed to cool, a few drops of $N/10$ sodium thiosulphate solution added, and heated to incipient boiling, when the flame is removed. Any ferric iron present is rapidly reduced on cooling. When the solution is water-white, potassium cyanide (1-2 c.c. of 10 per cent. solution) is added, and then ammonia until the solution just smells of it (excess should be avoided). After diluting in Nessler cylinders, 2 drops of colourless ammonium sulphide solution are added, and the colorations compared as described above.

In Germany, the following test, due to W. Klapproth, is used. 20 g. of the sample are ignited with 0·04 g. of calcium carbonate in a porcelain crucible. The small residue (which contains all the lead) is dissolved in a few drops of nitric acid, 2 or 3 drops of sulphuric acid added, and the mixture heated to expel the nitric acid. The residue, consisting of lead and calcium sulphates, is dissolved in ammonium acetate solution, and the solution filtered from insoluble matter (ferric oxide).

To the clear solution hydrogen sulphide water is added, and the resulting brown coloration compared with that of a solution of ammonium acetate in water, containing a known quantity of lead to which hydrogen sulphide water has been added under similar conditions. To make certain that the brown coloration is due to lead and not to copper, some potassium cyanide solution is added, which destroys the brown colour due to copper, but has no effect on that due to lead.

Other Tests.—Quantities of 3 g. of the acid are dissolved in water, and submitted to the following tests.

The solution of the pure acid should give no turbidity with barium chloride; nor, after the addition of nitric acid, with silver nitrate. The solution rendered alkaline with ammonia should give no precipitate with ammonium oxalate. The acid should require for titration the calculated quantity of normal alkali, which has been standardised by pure potassium hydrogen tartrate, using phenolphthalein as indicator, under exactly the same conditions of concentration.

Cream of Tartar.—This occurs in commerce in different grades of purity, containing varying proportions of calcium tartrate or calcium sulphate. The usual qualities are 95 per cent., 98 per cent., and 99-100

[1] *J. Soc. Chem. Ind.*, 1908, **28**, 636; Harvey and Wilkie, *Chem. and Drug.*, 1909, **75**, 92.

per cent. It is employed in dyeing as a mordant, for soupling silk, in food materials such as baking-powders, and in medicine. The tartaric acid and the contained calcium are determined.

The total tartaric acid is best estimated by the Goldenberg method.

The *Acidity*, on which the percentage of cream of tartar is generally gauged, is ascertained by titrating 5 g. of the sample with $N/1$ potassium hydroxide, which has been standardised by titration with 5 g. of pure recrystallised 100 per cent. cream of tartar, dried at 100°, under exactly the same conditions of concentration, using phenolphthalein as indicator. The titration can also be made with 2 g. of the cream of tartar with $N/5$ alkali, standarised under the same conditions as the actual test. This observance of exactly similar concentrations for standardisation and the actual test is necessary if exact results are to be obtained, owing to the hydrolysis of the neutral tartrate by water, which causes more alkali to be required (0·1-0·3 c.c.) in dilute solution than in concentrated solution.

To estimate tartaric acid rapidly in cream of tartar, baking-powders, etc., F. W. Richardson and J. C. Gregory,[1] and R. O. Brooks[2] have advocated a polarimetric method.

The requirements as regards *Arsenic* and *Lead* are the same as for tartaric acid.

Rochelle Salt (Sodium potassium tartrate) is employed in medicine, in silvering glass, and in electro-plating. The salt should dissolve in water to a clear solution, and the crystals also should be clear, where not rendered white on the surface by friction. The tests for purity are the same as for tartaric acid.

Tartar Emetic (Antimonyl potassium tartrate).—This is used as a fixative for tannin mordants in dyeing, and to a limited extent in medicine. For analysis, the salt is dissolved in 300 parts of warm water, the antimony precipitated by hydrogen sulphide, finally with addition of a little hydrochloric acid, and the liquid, separated by filtration from the antimony sulphide, used for the estimation of the tartaric acid. The antimony content is controlled by titration with iodine solution by Mohr's method (see the section on "Metals other than Iron," Vol. II., Part I., p. 282).

Neutral Potassium Tartrate, Borax Tartar, and **Iron Tartrate** find some application in medicine.

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[1] *J. Soc. Chem. Ind.*, 1903, **22**, 405.　　　　[2] *J. Amer. Chem. Soc.*, 1904, **26**, 813.

CITRIC ACID

By WILHELM KLAPPROTH, Dr Ing., Chemist to Messrs C. H. Boehringer, Nieder-
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I. RAW MATERIALS.

CITRIC acid is obtained from the juice of fruits of several species of
Citrus. Besides the juice of the lemon (*Citrus medica*), that of the
Bergamot (*Citrus Bergamia*) and of several West Indian species of
Citrus, especially the Lime (*Citrus Limonum*) are also worked. Small
quantities of citric acid were obtained experimentally some years back
by the fermentation of sugar by the organism discovered by C. Wehmer.[1]

The lemon juice is in general prepared at the place of production,
by pressing the fruit, and is then subjected to a short fermentation to
remove protein matter. The juice cleared in this way contains from
45-75 g. of citric acid per litre, and either comes direct into commerce,
or is further concentrated by boiling in open copper vessels. The price
for the juice per "pipe" is calculated on the basis of 64 oz. citric acid
per Imperial gallon. As 1 pipe = 108 Imperial gallons or 490 litres
(1 gallon = 4·536 litres), and 1 oz. = 28·35 g., the "pipe" of juice of the
above concentration contains 196 kg. of citric acid. Market prices are
referred to this unit. The concentrated bergamot juice is mostly sold
on the basis of 48 oz. per Imperial gallon. For factory purposes it is
often more useful to express the concentrations in grams per litre; the
above strengths of 64 and 48 oz. per gallon then become 400 g. and
300 g. of citric acid per litre.

Formerly such juice served exclusively as the raw material in the
manufacture of citric acid. Now, however, most of the juice is con-
verted into calcium citrate at the place of production, and this is to-day
the principal raw material. Raw lime juice is, however, still an
important article.

All analyses are expressed in terms of the tribasic citric acid with
1 mol. of water of crystallisation, *i.e.*, $C_6H_8O_7 + H_2O$, the molecular
weight of which = 210.

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[1] *Beiträge zur Kenntnis einheimischer Pilze*, i., 1893 ; Fabriques de produits chimiques de Thann
et Mulhouse, Ger. Pat. 72957, 1893 ; Eng. Pat., 5620, 1893, *J. Soc. Chem. Ind.*, 1894, **13**, 275.

The composition and complete analysis of raw juices have been studied by R. Warington[1] and more recently by K. Farnsteiner.[2]

The dark brown, concentrated juice was formerly valued either on its specific gravity, or on its acidity as determined by simple titration. Adulteration by salts (evaporated sea-water) and acids (*e.g.* sulphuric acid) was therefore common. The present method of analysis used in commerce was introduced by Warington, and is based on the insolubility of calcium citrate. It must be remembered, however, that calcium citrate is insoluble only in *hot* water, whilst it is not precipitated from a cold solution and even redissolves to a considerable extent in cold water.

Warington's method is now generally carried out as follows in this country and in Sicily (Ogston and Moore).

Calcium Citrate.

4 g. of the citrate is boiled with 30 c.c. of 2 N-hydrochloric acid in a 100 c.c. standard measuring flask for ten minutes, the solution being then cooled and made up to the mark with water. It is then shaken and filtered through a dry filter paper, 50 c.c. of the filtrate being measured by a standard pipette into a beaker of 300 c.c. capacity, and exactly neutralised with dilute sodium hydroxide free from carbonate, using phenolphthalein as indicator. The solution is next made slightly acid by the addition of 3 or 4 drops of N-hydrochloric acid, 2 c.c. of a 45 per cent. solution of calcium chloride added, the liquid raised to the boil and kept boiling for fifteen minutes; to avoid bumping it is necessary to stir the liquid well until actually boiling, after which it can safely be left. The hot liquid is filtered and the precipitate on the filter paper washed with boiling water six times. The filtrate and washings are then made just alkaline by adding a drop or two of dilute ammonia, and boiled down to about 15 c.c. The precipitate which forms is collected on a small filter paper and washed with *boiling* water six times, using a very small quantity of water for each washing. The filtrate and washings are treated with a drop of ammonia, if they have become acid, and are boiled down to about 10 c.c., but as a rule no further precipitate will be obtained whilst the liquid is hot; any precipitate which forms on cooling can be neglected.

The filter papers with their precipitates are dried at 100° and burnt together in a platinum dish with a cover. The flame should be kept low until the whole is charred, and then gradually raised until the ash is white. It is then carefully treated with 30 c.c. of N-hydrochloric acid, the whole boiled until all is dissolved and all carbon dioxide expelled, and the resulting solution titrated back with $N/5$ or $N/2$ sodium hydroxide, using phenolphthalein as indicator.

The sodium hydroxide is standardised by pure potassium hydrogen

[1] *J. Chem. Soc.*, 1875, 28, 925.　　　[2] *Z. Unters. Nahr. u. Genussm.*, 1903, 6, 1.

tartrate, and the $N/1$ hydrochloric acid by the alkali; phenolphthalein is used as indicator.

The number of cubic centimetres of $N/1$ HCl used for the neutralisation of the ash × 0·070 gives the weight of citric acid in the portion tested.

An almost identical method has been described by L. and J. Gadais.[1]

If the citrate contains much sulphate it is advisable to ash at as low a temperature as possible, preferably with an alcohol flame. Before dissolving in hydrochloric acid, the ash should be treated with 10 c.c. of hydrogen peroxide. [If, as is usual, the hydrogen peroxide contains free acid, allowance must of course be made for it.]

Lime Juice, Lemon Juice, and Factory Citric Acid Liquors.

The analysis of these materials is conducted as follows:—From 15-20 c.c. of unconcentrated juice, or an amount corresponding with 3 c.c. of concentrated juice (40 g. per 100 c.c.), previously diluted to facilitate exact measurement, are exactly neutralised with pure potassium hydroxide ($N/5$). The liquid, having a volume of about 50 c.c., is heated to boiling, mixed with a slight excess of concentrated calcium chloride solution, and kept at a gentle boil for half an hour. The precipitate is filtered off immediately while hot, washed with boiling water six times, and the mother liquor and washings again evaporated and worked up as described above under calcium citrate. The whole of the calcium citrate collected is then dissolved in 30 c.c. of $N/1$ hydrochloric acid and the excess of acid estimated as above. In dealing with the cruder factory liquors three or four evaporations are generally necessary to separate all the calcium citrate.

The above methods are not entirely free from error,[2] but have not yet been replaced by better. Incorrect results are obtained when the calcium citrate or juice contains other acids which yield sparingly soluble calcium salts. The presence of oxalic acid or of tartaric acid may be detected by the fact that the cold, neutralised solution gives a precipitate in the cold with calcium chloride.

C. Ulpiani and A. Parozzani[3] have described a method of analysis which, according to Klapproth, gives satisfactory results for citric acid even in presence of other organic acids. This method depends upon the fact that citric acid, in presence of a sufficient quantity of calcium chloride, is precipitated by sodium hydroxide *in the cold* when the whole of the acid is saturated, and in the *hot* solution when one-third of the acid is saturated. M. Spica[4] has described a method which consists in measuring the carbon monoxide which is evolved on gently warming

[1] *Bull. Soc. Chim.*, 1909 [iv.], **5**, 287.   [2] *Cf.* O. von Spindler, *Chem. Zeit.*, 1903, **27**, 1263.
[3] *Atti. R. Accad. Lincei*, 1906 [v.], **15**, ii., 517.
[4] *Chem. Zeit.*, 1910, **34**, 1141 ; *cf.* Barboni, *Ann. Lab. Centr. dell'e Gabelle*, 1912, p. 311.

the sample with concentrated sulphuric acid. Neither of these methods has been adopted in commerce.

The presence of sulphuric acid, which can give rise to error owing to the reduction of calcium sulphate to sulphide during ignition, may be recognised in the juice or liquors, after adding hydrochloric acid, by means of barium chloride. If only small quantities of sulphuric acid or sulphates are present, the above methods can be used; in presence of larger quantities, however, the use of hydrogen peroxide (see above) is necessary, or the following method proposed by J. Creuse[1] may be used :—

20 c.c. of the unconcentrated or 3 c.c. of the concentrated juice or liquor is accurately neutralised with pure (about $N/5$) potassium hydroxide and then evaporated to dryness on the water-bath. The residue is taken up with from 20-30 c.c. of 63 per cent. alcohol, and the potassium citrate filtered from the undissolved salts (potassium sulphate, etc.), the residue being washed with a little 93 per cent. alcohol. To the solution, which, if necessary, is neutralised with a drop of dilute acetic acid or ammonia, a neutral alcoholic solution of barium acetate is added and double the volume of 95 per cent. alcohol, the mixture vigorously stirred and left to the following day. The barium citrate precipitate, $(C_6H_5O_7)_2Ba_3$, is then filtered off and washed with 63 per cent. alcohol; the barium is estimated in the precipitate, after ignition, either by precipitation as barium sulphate or by dissolving it in $N/5$ hydrochloric acid and titrating back the excess of acid with alkali. As the precipitation of barium citrate presents certain difficulties, it is preferable, after the removal of the potassium sulphate by alcohol, to evaporate the latter, take up with a little water and precipitate with calcium chloride, subsequently igniting the calcium citrate and dissolving it in 30 c.c. of $N/1$ hydrochloric acid as in Warington's method. (W. A. D.)

To estimate *Free lime* or *Calcium carbonate* in calcium citrate, 5 g. of the sample is dissolved in a known quantity of standard hydrochloric acid ($N/1$ or $N/2$), kept gently boiling, and when cold the solution is titrated back with alkali hydroxide in the usual manner. Each cubic centimetre of normal acid neutralised by the sample corresponds with 0.050 g. $CaCO_3$ in the portion taken.

II. CONTROL OF WORKING CONDITIONS.

Although phosphoric acid, alumina, and iron are more readily removed from citric acid than from tartaric acid liquors, it is necessary, in order to avoid losses of citric acid, to see that the auxiliary materials as well as raw material are as free as possible from these substances.

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[1] *Chem. News*, 1872, **26**, 50.

The "impurity ratio" is determined as in the case of tartaric acid (see p. 289). Chalk and lime must be free from magnesia in treating juice, etc., otherwise not only is there loss of citric acid in the precipitation of the calcium citrate, but the citric acid liquors obtained from the latter will contain magnesium sulphate, which leads to subsequent loss.

Citric acid in the liquors is estimated by the methods given under I. Free sulphuric acid is estimated as in tartaric acid liquors (p. 291).

III. FINAL PRODUCTS.

Citric acid is used in dyeing and textile printing, and very largely for consumption in effervescent salines, lemonades, fruit essences, marmalades, bonbons, etc. On account of its pleasant, acid taste, it is particularly useful for the latter purposes, and it is also used in cake making. It is employed in medicine as a preventive of scurvy, gout, etc.

In view of differences in the amount of water of crystallisation contained by the acid, a titration of the acid is a useful test.

To detect and estimate *Oxalic Acid* the insolubility of calcium oxalate in *cold* solution is utilised ; calcium citrate is not precipitated in the cold.

To separate and estimate *Tartaric Acid* the insolubility of potassium hydrogen tartrate in alcohol is made use of, as in the Goldenberg method. (See p. 287.)

For detecting small quantities of tartaric acid in citric acid O. von Spindler utilises a colour reaction which is shown on precipitating citric acid solutions containing tartaric acid with a hot solution of mercuric oxysulphate mixed with potassium bichromate (Denigè's test).

A test proposed by P. Pusch consists in heating the acid with sulphuric acid for thirty seconds ; J. R. Will[1] has prepared a Table showing the different colorations produced by differing proportions of tartaric acid.

Lead, Arsenic, and *Ash* are tested for as under tartaric acid, the limiting quantities allowed being the same as in the case of tartaric acid. (See p. 293.) It is usual, however, in commerce to require a higher degree of freedom from lead than in the case of tartaric acid ; the amount present seldom exceeds 10 parts per million. Arsenic is generally entirely absent.

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[1] *Chem. Zeit.,* 1904, **28,** 15, 148.

ORGANIC PREPARATIONS

By J. MESSNER, Ph.D., Messrs E. Merck & Co., Darmstadt. English translation revised by CHARLES A. KEANE, D.Sc., Ph.D.

Acetaldehyde.

$$CH_3 . CQH. \quad \text{Molec. wt. } 44.03.$$

Acetaldehyde is a colourless, mobile, inflammable liquid. Sp. gr. 0.79; boiling point $21°$-$22°$. The purest commercial product (aldehyde absolutus) contains 95-98 per cent. of aldehyde, "aldehyde concentratissimus" about 80 per cent., and "aldehyde concentratus" about 60 per cent.

Acetaldehyde is miscible with water, alcohol, and ether in all proportions; also with ammonia when a considerable evolution of heat occurs. A yellowish-brown opalescence is produced on the addition of sodium hydroxide; ammoniacal silver solution is reduced on warming. An intense blue coloration is produced on adding a few drops of acetaldehyde to 10 c.c. of sodium nitroprusside solution mixed with 2-3 drops of piperidine; formaldehyde does not give this reaction.[1]

Tests for Impurities.

Inorganic Matter.—50 c.c. of the aldehyde should not leave more than 5 mg. of residue upon evaporation on the water-bath.

Metals.—Aldehyde should be neither coloured nor rendered turbid by sulphuretted hydrogen water or by the subsequent addition of ammonia till alkaline.

Hydrochloric acid. Chlorides.—No immediate change should take place on addition of silver nitrate solution.

Acetic Acid.—On addition of 2 c.c. of $N/1$ sodium hydroxide solution to 20 c.c. of aldehyde in 100 c.c. of water, the solution should be coloured red on addition of phenolphthalein. A good sample of aldehyde should not contain more than 0.6 g. of acetic acid in 100 c.c.

Quantitative Estimation.

The following method of estimation is due to R. Bourcart.[2] The

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[1] For colour reactions of aldehyde see *Z. anal. Chem.*, 1893, **32**, 347; 1898, **37**, 47; also *Merck's Reagenzien-Verzeichniss*, 1908, p. 289.

[2] *Bull. Soc. Ind. Mulhouse,* 1889, **59**, 558; *J. Soc. Chem. Ind.,* 1890, **9**, 557.

following solutions are prepared:—Potassium bichromate 1 : 100; sulphuric acid 10 per cent. by volume; potassium iodide 1 : 10; starch solution, and sodium thiosulphate solution of such a strength that 1 c.c. exactly corresponds to 1 c.c. of the above bichromate solution when titrated against it.

To carry out the determination 10 c.c. of the sample is made up to 1 litre with water, and 10 c.c. of the aldehyde solution placed in a well-fitted 100-125 c.c. pressure flask. To this solution 50 c.c. of the bichromate solution and 20 c.c. of the sulphuric acid are added, the flask closed and heated for three hours in a boiling water-bath. After cooling, the contents of the flask are washed out into a beaker, and sufficient potassium iodide solution added to produce a clear, brown solution, which is then titrated back with the thiosulphate. By the oxidation of aldehyde by means of chromic acid acetic acid is formed, 1 mol. of aldehyde requiring $\frac{1}{3}$ of a molecule of bichromate, or 1 mol. of bichromate oxidises 3 mols. of aldehyde. 1 c.c. of bichromate used up corresponds, therefore, to 0·004485 g. of aldehyde. In order to arrive at the percentage content of the aldehyde under examination, the number of cubic centimetres of bichromate solution used up is multiplied by 4·485, provided that the above quantities have been worked with.

This method is not applicable if the aldehyde contains alcohol, which is always the case with the poorer qualities. The following method is then preferable:—A 125 c.c. pressure flask is taken, in which are placed 30 c.c. of water, 20 c.c. of ammonia (sp. gr. 0·91), 25 c.c. of $N/1$ silver nitrate solution, and 25 c.c. of a freshly made solution of 2 c.c. of aldehyde in 100 c.c. of water. After closing the flask securely, it is heated for about eight hours in a boiling water-bath, allowed to cool, and the product of the reaction washed out into a 250 c.c. measuring flask which is finally filled up to the mark with water. After shaking well, the contents of the flask are allowed to settle, and 50 c.c. of the clear solution titrated with $N/10$ ammonium thiocyanate solution after acidifying with nitric acid and the addition of some iron alum solution as indicator. The quantity of silver solution decomposed by the aldehyde is thus determined. 1 c.c. $N/1$ silver nitrate solution corresponds to 0·022016 g. aldehyde.

The following method of analysis, due to A. Seyewetz and J. Bardin,[1] is applicable in the presence of alcohol, acetal, and paraldehyde. A few drops of phenolphthalein solution are added to a 10 per cent. solution of anhydrous sodium sulphite, which is then neutralised with sulphuric acid. To 40 c.c. of the neutral solution, which is cooled to 4° or 5°, 10 c.c. of a solution of acetaldehyde diluted to 7-8 per cent. is added, and the solution titrated with $N/1$ sulphuric acid till colour-

[1] *Bull. Soc. Chim.*, 1905 [iii.], **33**, 1000; *J. Soc. Chem. Ind.*, 1906, **25**, 202.

less. The content of aldehyde is calculated from the quantity of acid required for the titration according to the equation:—

$$2Na_2SO_3 + H_2SO_4 + 2CH_3COH = (NaHSO_3 + CH_3 . COH)_2 + Na_2SO_4.$$
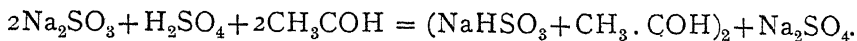
The following method is especially recommended:—About 20 c.c. of well-cooled water are placed in a 100 c.c. measuring flask, the whole tared on the balance and about 5 g. of acetaldehyde (accurately weighed) added. The flask is filled up to the mark with water, shaken, and 10 c.c. of the mixture transferred to a 500 c.c. stoppered flask containing about 350 c.c. of water and 30 c.c. of $N/1$ potassium hydroxide solution. After the addition of 10 c.c. of a 30 per cent. hydrogen peroxide solution (perhydrol) and thoroughly well shaking, the contents of the flask are allowed to stand overnight and then titrated with $N/1$ hydrochloric acid, using phenolphthalein as indicator. In addition, the acidity of the acetaldehyde must be determined and allowed for. For this purpose 10 g. of acetaldehyde are run into 50 c.c. of water and titrated with $N/1$ potassium hydroxide. 1 c.c. of potassium hydroxide corresponds to 0·04403 g. of acetaldehyde.

Acetanilide.

$$C_6H_5 . NH . COCH_3. \quad \text{Molec. wt. } 135·08.$$

Acetanilide crystallises in colourless glistening plates which dissolve in 230 parts of cold and in about 22 parts of boiling water, in 3·5 parts of alcohol, and readily in ether and chloroform; all the solutions have a neutral reaction. It has no smell and a slight burning taste. Acetanilide melts at 113°-114° and boils at 295°.

When heated with potassium hydroxide and a few drops of chloroform, acetanilide immediately gives the smell of isonitrile. When 0·1 g. of acetanilide are gently boiled for about half a minute with 2 c.c. of hydrochloric acid and 2 c.c. of a 5 per cent. aqueous solution of phenol, and sufficient calcium hypochlorite solution added, a reddish-violet turbidity is produced which changes to an indigo-blue solution on the addition of excess of ammonia.[1]

Tests for Impurities.

Inorganic Matter.—1 g. of acetanilide should, on heating, not leave more than 0·5 mg. of residue.

Foreign Organic Matter.—0·2 g. of acetanilide should dissolve to a colourless solution on shaking with 2 c.c. of sulphuric acid. This solution should not turn yellow on the addition of nitric acid (Phenacetine).

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[1] For other identifying reactions for acetanilide, cf. *Z. anal. Chem.*, 1888, **27**, 666; 1889, **28**, 103, 354, 709, 711; *Pharm. Zentralb.*, **30**, 241, 663; **32**, 41; *Pharm. Zeit.*, 1898, p. 546; *Merck's Reag.-Verz.*, 1908, p. 289.

The cold, saturated, aqueous solution of acetanilide should not be coloured by the addition of ferric chloride solution (aniline salts give a dirty green, antipyrine a red, salipyrine a violet, and thalline a green coloration).

Free Aniline, Dust, Resinous Matter, and Acet-toluide. may be recognised in the following manner :—A boiling solution of 1 g. of acetanilide in 30 c.c. of water, to which is added a drop of potassium permanganate solution (1 : 1000), should retain the rose coloration for at least five minutes, and on again boiling should not become either discoloured or cloudy. The commercial product cannot always be expected to comply to this stringent test. It is important that the glass vessel used for the test be scrupulously clean.

Free Acetic Acid.—The cold, saturated, aqueous solution of acetanilide should not redden blue litmus paper.[1]

Acetic Acid.

$$CH_3.COOH. \quad Molec. \ wt. \ 60.03.$$

Pure acetic acid comes into commerce of various strengths.

The 95-99 per cent. acid (glacial acetic acid) is a colourless liquid, with a suffocating acid smell, miscible in all proportions with water, alcohol, and ether. It has a sp. gr. of from 1·066-1·058 at 15°; it should not solidify above 9°·5, and should boil at 110°-117°. The completely anhydrous acid boils at 118° and has a sp. gr. of 1·0553 at 15°.

Tests for Impurities.

Inorganic Matter and non-volatile Organic Matter.—No appreciable residue should remain on evaporation of 10 c.c. of acetic acid.

Metals and Alkaline Earths.—20 c.c. of acetic acid, diluted with 100 c.c. of water, should show no brown coloration with sulphuretted hydrogen water. 10 c.c. of acetic acid, diluted with 100 c.c. of water, should remain unaltered on the addition of excess of ammonia, and also on allowing to stand in a warm place for some time after the addition of ammonium sulphide and of ammonium oxalate solution.

Arsenic.—2 c.c. of acetic acid to which is added 6 c.c. of stannous chloride solution should show no coloration on standing for an hour.

The Pharmacopœia Committee of the General Medical Council recommend the Gutzeit test as a limit-test for arsenic in acetic acid and other official substances. A special apparatus is described for

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[1] For the testing and valuation of acetanilide, *cf.* E. Ritsert, *Pharm. Zeit.*, 1890, 35, 306 ; *J. Soc. Chem. Ind.*, 1890, 9, 1068.

For the determination of acetanilide in pharmaceutical preparations, see J. L. Turner, and C. E. Vanderklud, *Pharm. J.*, 1907, p. 521 ; *J. Soc. Chem. Ind.*, 1907, 26, 486 ; also A. Seidell, *J. Amer. Chem. Soc.*, 1907, 29, 1088 ; *J. Soc. Chem. Ind.*, 1907, 26, 989.

carrying out the test and filter paper soaked in a saturated solution of mercuric chloride is used as the test-paper. The limit, in the case of acetic acid, is placed at 2 parts of arsenic per 1,000,000.[1] The Gutzeit test is described in the section on " Sulphuric Acid," Vol. I., Part I., p. 374.

Sulphuric Acid.—A solution of 10 c.c. of acetic acid in 150 c.c. of water heated to boiling, to which barium chloride solution is added, should show no formation of barium sulphate even on standing for several (fifteen) hours.

Hydrochloric Acid.—A solution of 5 c.c. of acetic acid in 50 c.c. of water should give no precipitate or opalescence on acidifying with 5 c.c. of nitric acid and adding silver nitrate solution.

Empyreumatic impurities and Sulphurous Acid.—0·3 c.c. of $N/10$ potassium permanganate solution should not be discoloured within a quarter of an hour by 5 c.c. of acetic acid diluted with 15 c.c. of water. A freshly made mixture of acetic acid and sulphuretted hydrogen water should remain clear.

Formic Acid.—If a mixture of 1 g. of acetic acid, 1 g. of sodium acetate, 10 c.c. of water, and 5 c.c. of mercuric chloride solution be heated for half an hour in a boiling water-bath, there should be no separation of mercurous chloride. Formic acid may be quantitatively estimated by the following method :—5 c.c. of the acetic acid are added to a solution of 5 g. of sodium acetate in 30 c.c. of water ; 40 c.c. of mercuric chloride solution (5 per cent.) are then added and the mixture heated for two hours in a steam-bath, using a reflux condenser. The separated mercurous chloride is collected in a Gooch crucible, washed with hot water, dried and weighed. The weight found multiplied by 0·097726 gives the quantity of formic acid.[2]

Acetic acid used for technical purposes, *e.g.* in the colour industry, need comply to but a few requirements, and the foregoing tests may therefore be correspondingly relaxed. (*Cf.* section on " Organic Dyes," Vol. II., Part II., p. 896.)

Quantitative Estimation.

1. By Titration.—The dilute aqueous solution of the acid is titrated with $N/1$ potassium hydroxide, using phenolphthalein as indicator. 1 c.c. of $N/1$ potassium hydroxide corresponds to 0·06003 g. of acetic acid.

2. A gas-volumetric method of estimation has been proposed by H. Kux.[3]

3. By the specific gravity as given in the subjoined Table prepared by A. Oudemans. On mixing concentrated acetic acid with water, a

[1] *Chem. and Drug.*, 1912, **81**, 122.   [2] Cf. *Apoth. Zeit.*, 1910, p. 727.
[3] *Z. anal. Chem.*, 1893, **32**, 138.

contraction in volume takes place with a corresponding rise in specific gravity, the latter attaining a maximum at a point corresponding to the formation of the hydrate, $C_2H_4O_2 + H_2O$ or ortho-acetic acid $[CH_3 . C(OH)_3]$. This hydrate contains 77 per cent. of acid, and has a sp. gr. of 1·0748. On further dilution the specific· gravity diminishes, so that a 51 per cent. acid has the same specific gravity as an acid of 97 per cent. Specific gravities above 1·0553 may therefore indicate acids of different strengths. In determining the strength of an acid by this method, the specific gravity is taken, and if it proves to be over 1·0553 the acid is diluted with not too much water. If on dilution the specific gravity rises, the acid is stronger than 77 per cent.; if the specific gravity diminishes, the acid is weaker than 77 per cent.

Table 39.

Specific Gravities of Acetic Acid at 15° (Oudemans).

Sp. gr.	Per cent.	Sp. gr.	Per cent.	Sp. gr.	Per cent.	Sp. gr.	Per cent.
1·0007	1	1·0363	26	1·0623	51	1·0747	76
1·0022	2	1·0375	27	1 0631	52	1·0748	77
1·0037	3	1·0388	28	1·0638	53	1·0748	78
1·0052	4	1·0400	29	1·0646	54	1·0748	79
1·0067	5	1·0412	30	1·0653	55	1·0748	80
1·0083	6	1·0424	31	1·0660	56	1·0747	81
1·0098	7	1·0436	32	1·0666	57	1·0746	82
1·0113	8	1·0447	33	1·0673	58	1·0744	83
1·0127	9	1·0459	34	1·0679	59	1·0742	84
1·0142	10	1·0470	35	1·0685	60	1·0739	85
1·0157	11	1·0481	36	1·0691	61	1·0736	86
1·0171	12	1·0492	37	1·0697	62	1·0731	87
1 0185	13	1·0502	38	1·0702	63	1·0726	88
1·0200	14	1·0513	39	1·0707	64	1·0720	89
1·0214	15	1·0523	40	1·0712	65	1·0713	90
1·0228	16	1·0533	41	1·0717	66	1·0705	91
1·0242	17	1·0543	42	1·0721	67	1·0696	92
1·0256	18	1·0552	43	1·0725	68	1·0686	93
1·0270	19	1·0562	44	1·0729	69	1·0674	94
1·0284	20	1·0571	45	1·0733	70	1·0660	95
1·0298	21	1·0580	46	1·0737	71	1·0644	96
1·0311	22	1·0589	47	1·0740	72	1·0625	97
1·0324	23	1·0598	48	1·0742	73	1·0604	98
1·0337	24	1·0607	49	1·0744	74	1·0580	99
1·0350	25	1·0615	50	1·0746	75	1·0553	100

Calcium Acetate.—The most important raw material in the manufacture of acetic acid is crude calcium acetate, which comes into the market as a grey to brown mass more or less contaminated with calcium carbonate and empyreumatic and decomposed organic matter. For its valuation, a determination of the content of pure calcium acetate or of acetic acid suffices. As a matter of practice the valuation may be limited to the estimation of the latter, by distillation with phosphoric

acid, according to the method given by R. Fresenius,[1] which is carried out as follows :—

A tubulated retort of suitable size, with its neck bent at an obtuse angle, is fitted air-tight to a Liebig's condenser. Into the retort is placed 5 g. of the calcium acetate to be tested, 50 c.c. of water, and 50 c.c. of phosphoric acid (free from volatile acids) of sp. gr. 1·2; the mixture is then heated on a sand-bath until all volatile products have distilled over, i.e. to dryness, and the distillate very carefully transferred to a 250 c.c. measuring flask. When the contents of the retort have cooled, 50 c.c. of water are added and a second distillation to dryness carried out. The same operation is repeated a third time, and finally the total distillate is made up to 250 c c., and 50 c.c. of the solution titrated with $N/1$ sodium hydroxide, using phenolphthalein as indicator. 1 c.c. $N/1$ sodium hydroxide corresponds to 0·06003 g. of acetic acid or 0·07907 g. of calcium acetate. The number of cubic centimetres of sodium hydroxide used multiplied by 6·003 gives the percentage content of acetic acid ($CH_3.COOH$), and multiplied by 7·907, the percentage content of anhydrous calcium acetate [$Ca(C_2H_3O_2)_2$].

The triple distillation as given above may be dispensed with by somewhat modifying the procedure as follows :—The tubulated retort is connected up with a suitable steam supply, which may be readily connected and disconnected and the steam led into the bottom of the retort by means of a bent glass tube. As soon as the bulk of the volatile matter has come over on the sand-bath, steam is allowed to blow in through the thick residue, at the same time reducing the heat of the sand-bath. For the distillation by steam a 500 c.c. measuring flask is used as receiver. The distillation is stopped as soon as the distillate ceases to be acid. The receiver is then filled up to the mark with water and the contents well mixed by shaking. When working on 5 g. of the crude acetate and using the data for calculation given above, 100 c.c. of the acetic acid solution obtained by distillation is titrated.

In this method of estimating acetic acid, small quantities of homologous acids (propionic, butyric, etc.) contained in the calcium acetate are determined along with the acetic acid and calculated as such. This source of error is generally a matter of little importance in technical work, but should it be desired to take these acids into account, the method given by E. Luck[2] is recommended, which is based on the

[1] Z. anal. Chem., 1866, 5, 315 ; 1875, 14, 172. Cf. also W. Fresenius and L. Grünhut, ibid., 1908, 47, 597 ; J. Soc. Chem. Ind., 1908, 27, 1012 ; J. Jedlicka, ibid., 1910, 49, 97 ; J. Soc. Chem. Ind., 1910, 29, 421 ; and T. S. Gladding, J. Ind. and Eng. Chem., 1909, 1, 250 ; J. Soc. Chem. Ind., 1909, 28, 467.

[2] Z. anal. Chem., 1871, 10, 184 ; cf. also Pharm. Zeit., 1910, p. 810.

different solubilities of the barium salts of these homologous acids in absolute alcohol.

To carry out this method the distillate obtained in the manner previously given is neutralised with barium hydroxide, evaporated to dryness, and well boiled with 800 c.c. of absolute alcohol. The alcoholic solution, which contains the barium salts of the homologous acids and 0·0284 g. of barium acetate per 100 c.c., is cooled and filtered, the alcohol evaporated off, the residue taken up with water, the barium precipitated with sulphuric acid, and the barium sulphate weighed. From the weight of the latter, 0·2085 g. must be subtracted to allow for the barium acetate (as barium sulphate) dissolved by the 800 c.c. of alcohol, and the remaining barium sulphate calculated to calcium acetate (1 g. barium sulphate = 0·6774 g. calcium acetate). The quantity of calcium acetate thus found is deducted from the amount found by titration.

If the calcium acetate to be examined contains appreciable quantities of calcium chloride, the distillate obtained by the foregoing methods will contain hydrochloric acid. A portion of the distillate is therefore tested for chloride by adding nitric acid and silver nitrate solution. If only an opalescence is produced, the trace of hydrochloric acid may be neglected, but if a precipitate of silver chloride be formed, the hydrochloric acid must be estimated either volumetrically with $N/1$ silver nitrate solution or by weighing the precipitate of silver chloride, and the quantity found allowed for.

Acetone.[1]

$$CH_3 . CO . CH_3. \quad \text{Molec. wt. } 58·05.$$

Acetone is a colourless, mobile, neutral liquid, readily inflammable, burning with a luminous non-smoky flame. It has a peculiar, not unpleasant smell and a camphor-like taste. Acetone boils at 55°-56°, and has a sp. gr. of 0·798. It is miscible with water, alcohol, ether, chloroform, and oils in all proportions. When 10 c.c. of acetone are mixed with 10 c.c. of ammonia, which should produce no warming of the solution (aldehyde), then 10 c.c. of $N/1$ iodine solution added and the mixture diluted with 60 c.c. of water, a cloudiness due to the formation of iodoform is produced.[2]

Tests for Impurities.

Non-volatile Matter.—On evaporation, 25 c.c. of acetone should leave no residue.

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[1] *Cf.* the section on " Explosives," Vol. II., Part I., pp. 492 *et seq.*

[2] For identifying and colour reactions, cf. *Pharm. Zentralh.*, 36, 616 ; 37, 439 ; *Z. anal. Chem.*, 1893, 32, 347 ; 1898, 37, 47 ; *Chem. Zeit.*, 1909, 33, 570 ; and *Merck's Reag.-Verz.*, 1908, p. 289.

Free Acid.—Blue litmus paper should not be reddened.

Empyreumatic Matter.—A mixture of equal parts of acetone and water should be clear.

Aldehyde.[1]—A mixture of 10 c.c. of acetone and 5 c.c. of ammoniacal silver solution is warmed for fifteen minutes in a water-bath at 50°, the test being carried out in the dark. No darkening of the solution or separation of metallic silver should take place. (The silver solution for this test is prepared by mixing 10 c.c. of a 5 per cent. silver nitrate solution with 5 c.c. of 10 per cent. ammonia.)

Action of Potassium Permanganate.—10 c.c. of acetone to which is added a drop of potassium permanganate solution (1 : 1000) should retain the pink colour for at least fifteen minutes at a temperature not above 15°. By this test the presence of aldehyde is indicated.[2] The usual requirement in this country is that a distinct colour should remain for thirty minutes when 1 c.c. of a 0·1 per cent. pure permanganate solution is added to 100 c.c. of acetone at 15°·5. Acetone containing 0·5 per cent. by volume of aldehyde discolours the permanganate in five minutes, and if it contains 0·25 per cent. by volume of aldehyde, the discoloration is complete in ten minutes. Free mineral acids should not be present, since these discharge the permanganate colour in the case of aldehyde-free acetone.

Water.—30 c.c. of acetone are shaken in a closed flask with ignited potassium carbonate, when the latter should show no signs of becoming damp. On mixing 50 c.c. of acetone with 50 c.c. of petroleum spirit (boiling point 40°-60°) no indication of the separation of the liquid into two layers should be visible.

Quantitative Estimation.

G. Krämer has worked out a method for determining acetone in methyl alcohol, which may be equally well applied to its estimation in commercial acetone. For this purpose acetone is diluted with 9 parts of water, sufficient sodium hydroxide solution and iodine solution added, and the mixture extracted with an accurately measured quantity of ether, which dissolves out the iodoform formed. An aliquot part of the ethereal solution is then evaporated off on a weighed clock-glass, the residue dried over sulphuric acid and weighed. From the weight of iodoform found the content of acetone is calculated ; 3·94 g. of iodoform correspond to 0·58 g. of acetone.[3]

Volumetric modifications of this method are described below under

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[2] For the detection of aldehyde, *cf.* also *Z. anal. Chem.*, 1883, **22**, 259 ; 1891, **30**, 208 ; 1895, **34**, 226.

[3] *Ber.*, 1880, **13**, 1000. On a source of error in this method of estimation, *cf.* Vaubel and Scheuer, *Z. angew. Chem.*, 1905, **18**, 214.

the estimation of acetone in methyl alcohol (p. 364) and in the section on " Explosives," Vol. II., Part I., p. 493.

H. Strache[1] has proposed a method which consists in converting the ketone, in sodium acetate solution, into the hydrazone by means of an excess of phenylhydrazine. The hydrazone is not acted upon by Fehling solution, but the excess of phenylhydrazine is decomposed by hot Fehling solution giving up its nitrogen completely, which latter may be determined gas-volumetrically. The nitrogen found gives the unused phenylhydrazine; the used phenylhydrazine is obtained by difference, from which data the acetone can be calculated.[2]

Acetyl Salicylic Acid (Aspirin).

$$C_6H_4 \begin{cases} O . COCH_3 (1) \\ COOH (2) \end{cases} . \qquad \text{Molec. wt. } 180.06.$$
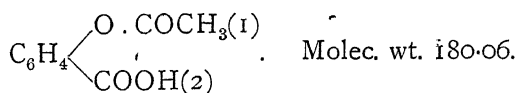
Acetyl salicylic acid forms small white crystalline needles possessing a slightly acid taste, which dissolve in 300 parts of water, readily in alcohol and in sodium hydroxide and sodium carbonate solutions. Melting point, 175°.

When 0.5 g. of acetyl salicylic acid is boiled for two to three minutes with 10 c.c. of sodium hydroxide and, after cooling, dilute sulphuric acid added, a transitory violet coloration is first produced, and then a white crystalline precipitate of salicylic acid separates out. If the precipitate is filtered off, the filtrate smells of acetic acid, and on boiling with a little alcohol and sulphuric acid gives the characteristic smell of ethyl acetate.

Tests for Impurities.

Salicylic Acid.—A solution of 0.1 g. of acetyl salicylic acid in 5 c.c. of alcohol, prepared in the cold, to which 20 c.c. of water are added, should not give an immediate violet coloration on the addition of a drop of ferric chloride solution.

Hydrochloric and Sulphuric Acids.—If 1 g. of acetyl salicylic acid is shaken for five minutes with 20 c.c. of water, the filtrate should remain clear on the addition of silver nitrate and of barium nitrate solutions.

Organic Impurities.—1 g. of acetyl salicylic acid should dissolve to a colourless solution in 10 c.c. of concentrated sulphuric acid.

Inorganic Impurities.—On burning off 1 g. of acetyl salicylic acid, no appreciable residue should be left.

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[1] *Monatsh.*, 1891, **12**, 524 ; *Z. anal. Chem.*, 1892, **31**, 573.

[2] For detecting and estimating wood spirit in acetone, *cf.* F. W. Babington, *J. Soc. Chem. Ind.*, 1907, **26**, 243.

For the quantitative estimation of acetone in crude acetone, *cf.* G. Heikel, *Chem. Zeit.*, 1908, **32**, 75 ; *J. Soc. Chem. Ind.*, 1908, **27**, 114 ; and S. J. M. Auld, *J. Soc. Chem. Ind.*, 1906, **25**, 100.

Quantitative Estimation.

1 g. of acetyl salicylic acid is boiled for three minutes with 15 c.c. of $N/1$ sodium hydroxide solution, allowed to cool, and then titrated with $N/1$ hydrochloric acid, using phenolphthalein as indicator; 3.9 c.c. of $N/1$ hydrochloric acid should be necessary to discharge the red colour. 1 c.c. of $N/1$ sodium hydroxide corresponds to 0.09003 g. of acetyl salicylic acid.

Amyl Acetate.

$$CH_3 . COOC_5H_{11}. \quad \text{Molec. wt. } 130.11.$$
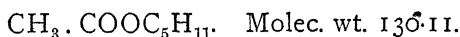
Amyl acetate (isoamyl acetate) is a colourless, mobile, peculiar smelling liquid. Chemically pure amyl acetate has a sp. gr. of 0.8692, and boils at 138°. The commercially pure products which come on to the market have a sp. gr. of 0.867-0.869, and boil between 135°-142°.

Amyl acetate dissolves readily in alcohol, ether, benzene, chloroform, and glacial acetic acid, but is quite insoluble in water.

Tests for Impurities.

Inorganic and non-volatile Organic Compounds.—10 c.c. of amyl acetate should not leave more than 0.5 mg. of residue on evaporation.

Hydrochloric Acid and Sulphuric Acid.—On shaking 30 c.c. of amyl acetate with 15 c.c. of water, the separated water should at most only give a slight opalescence with silver nitrate solution, and should show nothing with barium chloride solution, even on standing for some time. (The separated water always reacts acid on account of the presence of small quantities of free acetic acid.)

Alcohol.—On shaking 25 c.c. of amyl acetate with 25 c.c. of a saturated calcium chloride solution and allowing the liquids to separate completely, the calcium chloride solution should, at most, show an increase in volume not greater than 1 c.c.

Note.—Amyl acetate comes into commerce in 10 per cent. alcoholic solution, as pear oil. On treating such a product with calcium chloride solution it gives up about 90 per cent. of its volume to the latter; for this reason it is better to shake up with a proportionally large volume of calcium chloride solution. It is generally sufficient in dealing with such products to only take notice of the content of amyl acetate. The content of alcohol cannot be judged from the specific gravity, since alcohol of 75-76 per cent. by volume has the same specific gravity as amyl acetate.

Water.—Amyl acetate should dissolve to a clear solution when mixed with ten times its volume of benzene. The purest, anhydrous amyl acetate mixes in the same proportion (1 : 10) with petroleum spirit

and with official paraffin oil (liquid paraffin), producing perfectly clear solutions. The test with the latter is specially sensitive.

Amyl Nitrite.

$$(CH_3)_2CH . CH_2 . CH_2 . O . NO. \quad \text{Molec. wt. } 117.10.$$
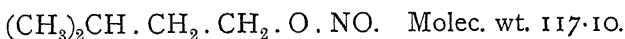
Amyl nitrite is a clear yellow liquid with a fruity smell. It is quite insoluble in water, but mixes with alcohol and ether in all proportions. Authorities differ as to the boiling point; Hilger gives 94°-95°, Bernthsen 96°, Dunstan and Williams[1] 97°, Chapman[2] 97°-98°, and Guthrie[3] 99°. Dunstan and Williams give a sp. gr. of 0.880, Hilger of 0.902, the British Pharmacopœia of 0.870-0.880, and the German Pharmacopœia of 0.875-0.885. The commercial preparations generally have a lower boiling point than given above. A sample, however, which begins to boil at 90° cannot be pure, even if it otherwise conforms to requirements, whilst a sample boiling above 99° points to a too high content of amyl alcohol. It is to be borne in mind that amyl nitrite continually undergoes slow decomposition, which may account for variations in the boiling point and specific gravity as well as in the content of acid and of amyl alcohol.

Amyl nitrite burns with a yellow, luminous, smoky flame. On the addition of hydrochloric acid and a few crystals of ferrous sulphate a brown coloration is produced.

Tests for Impurities.

Free Nitrous Acid.—A mixture of 1 c.c. of water, 0.1 c.c. of ammonia (sp. gr. 0.96), and 2 drops of tincture of litmus shaken up with 5 c.c. of amyl nitrite should not be reddened; this indicates a maximum content of about 0.35 per cent. of nitrous acid.

Valeryl Aldehyde.—A mixture of 1 c.c. of amyl nitrite, 1.5 c.c. of silver nitrate solution, 1.5 c.c. of absolute alcohol, and a few drops of ammonia should not be turned brown or black on gently warming.

Water.—Amyl nitrite should not become turbid when cooled down to 0°.

Ethyl Alcohol.—10 c.c. of water and 10 c.c. of amyl nitrite are shaken up in a graduated measuring cylinder. If alcohol is present in not too small a quantity, the volume of water increases. The separated water will give the iodoform reaction.

Quantitative Estimation.

Amyl nitrite may be estimated volumetrically in various ways.

[1] *Pharm. J.,* 1888, 19, 487.   [2] *Laboratory,* 1867, p. 375.
[3] *J. Chem. Soc.,* 1859, 11, 245.

The method given for estimating ethyl nitrite, by E. Schmidt,[1] may be applied, as also that by Curtmann.[2]

The best and simplest method is the gas-volumetric estimation, which is carried out as follows :—26 g. of amyl nitrite are diluted with 91 per cent. alcohol to 500 c.c. in a measuring flask. 5 c.c. of the dilute alcoholic solution are introduced into a nitrometer (Vol. I., Part I., p. 132), and 10 c.c. of potassium iodide solution (1 : 5) and then 10 c.c. of $N/1$ sulphuric acid added. The volume of nitric oxide evolved is measured and corrected for temperature and pressure. It generally suffices when reading off the volume at about 20° to reckon every cubic centimetre of gas as equivalent to 2 per cent. of amyl nitrite. A good sample of amyl nitrite would liberate at least 40 c.c. of nitric oxide, equivalent to 80 per cent. of amyl nitrite, whilst a pure 100 per cent. sample would yield 50 c.c. The reaction proceeds according to the following equation :—

$$C_5H_{11}NO_2 + KI + H_2SO_4 = I + KHSO_4 + C_5H_{11}OH + NO.$$
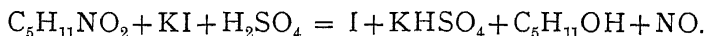
At normal pressure, 1 c.c. of nitric oxide at 0° weighs 0·0013402 g. If it is desired to take accurate readings, the volume found is reduced to 0° and 760 mm. pressure by the following formula :—

$$V_0 = \frac{760 \cdot (1 + 0·0366t)}{V_1 \cdot b},$$

where V_0 is the corrected volume at 0°, V_1 is the observed volume, b the observed atmospheric pressure, and t the observed temperature.

The following quite good method for the estimation of amyl nitrite is prescribed by the Dutch Pharmacopœia :—0·5 g. of amyl nitrite are dissolved in 10 c.c. of alcohol, and 15 c.c. of an aqueous solution of potassium chlorate (1 : 20) and 5 c.c. of nitric acid (sp. gr. 1·316) added. The mixture is allowed to react for one hour, with frequent shaking. Then 20 c.c. of $N/10$ silver nitrate solution and 5 drops of an aqueous, saturated solution of ferric ammonium sulphate are added, and the excess of silver nitrate determined by titration with $N/10$ ammonium thiocyanate solution. Not more than 8·6 c.c. of the thiocyanate solution should be required to produce a red coloration; this condition corresponds to a minimum content of 80 per cent. of amyl nitrite. 1 c.c. of $N/10$ silver nitrate solution = 0·0351 g. of $C_5H_{11}NO_2$.

Apomorphine Hydrochloride.

$C_{17}H_{17}O_2N \cdot HCl.$ Molec. wt. 303·61.
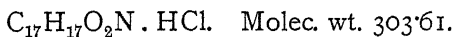
Apomorphine hydrochloride crystallises in small white or grey crystals which are soluble in about 50 parts of water and 40 parts

[1] *Pharmazeutische Chemie.,* 3rd edition, vol. ii., p. 567.
[2] *Cf.* Südd, *Apoth. Zeit.,* 1898, p. 716 ; also *ibid.,* 1896, pp. 66 and 305, for a description and criticism of different methods of estimation.

of alcohol (of about 85 per cent. by weight). It is quite insoluble in ether and chloroform. The solutions react neutral with litmus paper and gradually turn green on standing in the light and in air; if some hydrochloric acid, however, is added to the solutions they remain unchanged for a longer time, but the addition of too much hydrochloric acid causes apomorphine hydrochloride to separate out. On standing over sulphuric acid, apomorphine hydrochloride gradually loses in weight to the extent of about 3·6 per cent. The salt dried in this way regains its original weight on exposure to the air.

Apomorphine hydrochloride dissolves in nitric acid, producing a blood-red coloration. The addition of a drop of very dilute ferric chloride solution to an aqueous solution of the salt (1 : 10,000) turns the latter blue. If to 10 c.c. of an aqueous solution (1 : 10,000) 1 c.c. of chloroform is added, and after the addition of sodium hydroxide solution the mixture is immediately shaken with air, the aqueous liquid assumes a transitory reddish-violet, and the chloroform a blue coloration. Silver nitrate solution produces with an aqueous solution of the salt, after the addition of a drop of nitric acid, a white curdy precipitate which is blackened immediately on the further addition of ammonia.

Tests for Impurities.

Oxidation Products of Apomorphine.—A freshly prepared solution (1 : 100 of water) should be colourless or only very faintly coloured. 5 c.c. of ether shaken with 0·1 g. of dry apomorphine hydrochloride should remain colourless or show only a very faint pink coloration.

Other Alkaloids.—If 0·1 g. of apomorphine hydrochloride be placed on a small, dry filter paper, and 5 c.c. of a mixture of 1 c.c. of hydrochloric acid with 4 c.c. of water poured over it, on addition of potassium-mercuric iodide solution to the filtrate, at most only an opalescent turbidity should be produced.

β-Chloro-morphide.—0·1 g. of apomorphine hydrochloride is dissolved in 10 c.c. of water, 20 c.c. of ether poured on, 5 c.c. of a cold, saturated solution of sodium carbonate added, and the mixture shaken until the precipitate which is first formed redissolves. The aqueous solution is run off, the ether well washed three times with about 20 c.c. of water, and then completely evaporated off in a test tube. To the cooled residue 5 c.c. of concentrated nitric acid containing 0·5 per cent. of silver nitrate are added, and after standing for ten minutes the test tube is placed in a boiling water-bath for one hour. At the end of this time there should be no appreciable flakes of silver chloride at the bottom of the clear, undiluted brown liquid.[1]

[1] *Pharm. Zentralh.*, 1911, **52**, 537 ; *J. Soc. Chem. Ind.*, 1911, **30**, 1278.

Inorganic Impurities.—On ignition, 1 g. of apomorphine hydro-chloride should not leave more than 0·5 mg. of residue.[1]

Atropine.

$C_{17}H_{23}O_3N$.   Molec. wt. 289·19.

Atropine crystallises in small, colourless needles which dissolve in about 300 parts of water and which are readily soluble in alcohol (90 per cent), ether, and chloroform.   Melting point, 115°·5.

Tests and Quantitative Estimation.

Hyoscyamine.—The free base should be optically inactive.   The more hyoscyamine it contains the more lævorotatory will it be.   (The rotatory power of hyoscyamine is $(a)_D = -20°·97$.)

The tests for inorganic and organic impurities as well as for foreign alkaloids are carried out as described below for atropine sulphate.

To estimate atropine volumetrically, about 0·1 g. is dissolved in 50 c.c. of absolute alcohol, some pure lackmoid[2] added, and the solution titrated with $N/10$ hydrochloric acid until the blue colour changes to red.   1 c.c. of $N/10$ hydrochloric acid corresponds to 0·02892 g. of atropine.

Atropine Sulphate.

$(C_{17}H_{23}O_3N)_2H_2SO_4 + H_2O$.   Molec. wt. 694·49.

Atropine sulphate comes into commerce in white crystalline masses (small crystalline needles).   The melting point depends on the con-ditions under which it is taken.   If Roth's apparatus be used, and the temperature raised very slowly, the best commercial product dried over sulphuric acid gives a melting point of 185°; if heated quickly, the melting point is higher, and the same product may be found to give a melting point as high as 190°.   These differences point to the melting point of atropine sulphate being in reality a decomposition point.   The melting point given by the British Pharmacopœia is 183°.   In doubtful cases it is safest to prepare the gold chloride double salt and to take its melting point, which in the case of a good preparation should not be above 138°.   According to the instructions of the German Pharmacopœia the melting point of the free base is determined.   For this purpose ammonia is added to the aqueous solution of atropine sulphate (1 : 25), the crystals which separate on standing collected on a small filter paper, washed with water and dried over sulphuric acid ; they should melt at 115°.

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[1] On doubtful modern commercial preparations of apomorphine, *cf.* Harnack and Hilde-brandt, *Pharm. Zeit.*, 1909, 54, 938 ; 1910, 55, 6 and 693.   On apomorphine hydrochloride substi-tutes, see Frerichs, *Apoth. Zeit.*, 1909, p. 928.

[2] *Z. angew. Chem.*, 1903, 16, 449, 468.

Atropine sulphate, which dissolves readily in water and alcohol to a colourless neutral solution, is difficultly soluble in ether, benzene, and chloroform.

If 0·01 g. of atropine sulphate is evaporated to dryness on a water-bath with fuming nitric acid, a pale yellow residue is left, which, when cold, produces a violet coloration on the addition of alcoholic potash.[1]

Tests for Impurities.

Inorganic Matter.—On ignition, 0·1 g. of atropine sulphate should not leave more than 0·5 mg. of residue.

Organic Impurities.—0·1 g. of atropine sulphate should dissolve without coloration in 5 c.c. of sulphuric acid.

Other Alkaloids.—The solution in sulphuric acid should remain colourless on the addition of nitric acid. The aqueous solution of atropine sulphate (0·1 : 6) should not be rendered turbid by ammonia.

Hyoscyamine.—The free base obtained from the aqueous solution by the addition of alkali and extraction with ether should, after drying, give the melting point of atropine and be inactive in alcoholic solution.

Water.—1 g. of atropine sulphate should not lose more than 0·026 g. in weight on drying at 100°.

Atropine sulphate may be titrated in pure alcoholic solution with $N/10$ sodium hydroxide, using Poirrier's blue as indicator, and excluding carbon dioxide from the air.[2] (*Cf.* Quinine hydrochloride, p. 381.)

Benzaldehyde.

$$C_6H_5 . COH. \quad \text{Molec. wt. } 106·05.$$

Benzaldehyde is a colourless, highly refractive liquid with a characteristic smell. It boils at 177°-179°, and has a sp. gr. of 1·046-1·054. It dissolves readily in alcohol, ether, benzene, chloroform, and petroleum spirit, but only sparingly in water (about 1 in 300 parts).

Tests for Impurities.

Inorganic Matter.—On heating, benzaldehyde burns with a very smoky flame, and leaves no residue on ignition.

Chlorine.—2 g. of benzaldehyde are put into a small porcelain crucible, which is placed on a porcelain plate of suitable size. The benzaldehyde is ignited with a Bunsen burner, and a 2 litre beaker, the inside of which is moistened with water, is placed over the burning benzaldehyde, and is lifted now and again from the plate so as to regulate the supply of air. It is well to extinguish the flame a few

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[1] For other identifying reactions, *cf. Merck's Reag.-Verz.*, 1908, p. 290.
[2] For further details, cf. *Z. angew. Chem.*, 1903, **16**, 470.

times and re-moisten the beaker before re-lighting. When all the benzaldehyde is burnt in this manner, the beaker and plate are washed with a little water, which is then filtered through a small filter paper, and the filter paper washed with water until a filtrate of 20 c.c. is obtained. After acidifying the filtrate with a few drops of nitric acid, silver nitrate solution is added which should only produce a very faint opalescence.

Synthetically prepared benzaldehyde is never absolutely free from chlorine.

Organic Chloride (*e.g.* Benzyl chloride).—10 g. of benzaldehyde are subjected to distillation, and the first 10-12 drops that come over are collected in 5 per cent. alcoholic potash. This solution is then heated for some time, using a reflux condenser, and the alcohol finally evaporated off. The residue is taken up with water, shaken with ether to remove oily products, nitric acid added to the aqueous solution after pouring off the ether, and the separated benzoic acid filtered off. The filtrate is tested for chlorine with silver nitrate solution as above.

Chloro-benzaldehyde.—2 c.c. of benzaldehyde are shaken with 40 c.c. of water, 6 g. of sodium carbonate (free from chlorine) added, the mixture gently heated, and 5 per cent. potassium permanganate solution (free from chloride) added gradually until the smell of oil of bitter almonds has completely disappeared. If the red coloration due to permanganate does not also disappear, alcohol is added, drop by drop, until the solution is colourless. The mixture is filtered and dilute sulphuric acid (free from chlorine) added. When quite cold, the separated benzoic acid is collected on a filter paper, washed with cold water, dissolved in sodium carbonate solution, and after the addition of potassium nitrate evaporated to dryness and ignited. The ignited residue is dissolved in water and nitric acid, made up to 20 c.c., and tested for hydrochloric acid with silver nitrate as above.

Nitrobenzene.—2 drops of phenol, 3 drops of water, and a piece of potassium hydroxide the size of a pea are placed in a small porcelain dish. The mixture is heated carefully to boiling, and then the benzaldehyde under examination, shaken up with water, added. After keeping at the boil for some time a carmine red ring appears at the edges of the liquid. On the addition of a saturated solution of calcium hypochlorite the colour of the ring changes to emerald green in the presence of nitrobenzene.[1] If present in appreciable quantities, nitrobenzene raises the specific gravity of benzaldehyde. 5 c.c. of pure benzaldehyde at 12°·5 weigh from 5·2055-5·222 g.; if it contain 25 per cent. of nitrobenzene the weight of 5 c.c. becomes 5·39 g.; and if 50 per cent., 5·57 g.

A further test for nitrobenzene is carried out as follows:—1 g. of

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[1] Marpurgo, *Pharm. Zeitschr. f. Russland*, vol. 29, p. 205.

benzaldehyde, dissolved in 20 c.c. of alcohol, is diluted with water until a permanent turbidity is produced. Granulated zinc and sulphuric acid are then added. When the evolution of hydrogen has ceased, the solution is filtered, the alcohol evaporated off, and the aniline formed from the nitrobenzene detected as follows :—To half the filtrate, a few drops of potassium bichromate solution is added and the solution boiled for a short time ; in the presence of aniline a pale violet coloration is produced. The other half of the filtrate is neutralised with potassium hydroxide, and sodium hypochlorite added ; if aniline be present a violet coloration is formed.

Alcohol.—If 20 c.c. of benzaldehyde are shaken up with 20 c.c. of a cold, saturated solution of calcium chloride, the volume of the latter should not be found to have increased after completely separating the liquids. If 3 c.c. of benzaldehyde are mixed with 10 c.c. of nitric acid (sp. gr. 1·4) the presence of alcohol will cause an evolution of gas and of red fumes.

Water.—Benzaldehyde should dissolve to a perfectly clear solution in ten times its volume of petroleum spirit (boiling point 50°-75°).

Benzoic Acid.—Benzaldehyde always contains some benzoic acid, since it readily oxidises in presence of air. In the purest commercial product 1-3 per cent. is not uncommon. Up to 14 per cent. of the acid remains dissolved in the benzaldehyde at 15°, but if the proportion be larger it crystallises out. To estimate the benzoic acid, 10 g. of benzaldehyde are dissolved in 50 c.c. of dilute alcohol (70 per cent. by volume), and the solution titrated with $N/1$ sodium hydroxide solution (1 c.c. = 0·122048 g. benzoic acid), using phenolphthalein as indicator.

Hydrocyanic Acid.—2 c.c. of benzaldehyde are shaken with 20 c.c. of $N/1$ potassium hydroxide solution, a few drops of ferrous sulphate solution added, and the mixture heated nearly to boiling. Hydrochloric acid is then added in excess, and then a drop of ferric chloride solution. If hydrocyanic acid be present it will be recognised by the formation of Prussian blue.

Hydrocyanic acid occurs in oil of bitter almonds, and can therefore be found in benzaldehyde prepared from this source. Oil of bitter almonds itself usually comes on to the market, labelled either "free from prussic acid" or "containing prussic acid." The oil of bitter almonds "free from prussic acid" is not poisonous. Natural oil of bitter almonds containing prussic acid can be distinguished from the chemically prepared benzaldehyde by a method due to A. Kremel,[1] according to which oil of bitter almonds containing prussic acid yields benzoin, without the addition of potassium cyanide, whilst the chemically prepared benzaldehyde does not.

[1] *Pharm. Zentralh.,* **30,** 134.

Benzoic Acid.

$C_6H_5 . COOH.$ Molec. wt. 122·05.

Two varieties of benzoic acid come on to the market, the official benzoic acid prepared from gum benzoin, and the chemically pure product prepared from either benzyl chloride, benzal chloride, benzotrichloride or hippuric acid.

(a) Official Benzoic Acid.

This is sublimed from Siamese gum benzoin, and forms small white or brown leafy or needle-like crystals of a silky appearance, which possess a characteristic burning smell. It melts at 120°, and boils at 249°.

Benzoic acid dissolves in 270 parts of water at 15° and readily in hot water, in ether, alcohol, benzene, chloroform, petroleum spirit, and carbon bisulphide.

On shaking 0·2 g. of benzoic acid frequently during fifteen minutes with a mixture of 1 c.c. of $N/1$ potassium hydroxide solution and 20 c.c. of water, filtering, and adding to the filtrate a drop of ferric chloride solution, a reddish-brown to dirty red precipitate is produced.

Tests for Impurities.

Official benzoic acid should melt in boiling water, when more acid is used than will dissolve in the quantity of water taken. Chemically prepared benzoic acid does not melt under these conditions.

Inorganic and foreign Organic Matter.—On heating 0·2-0·3 g. of benzoic acid in a test tube, it first melts to a yellow then to a brown mass, and then sublimes, and should finally leave either no residue or only a very slight brown residue. No charring should take place; should this occur it would point to the presence of sugar, hippuric, tartaric, or citric acids.

Salicylic Acid.—An aqueous solution of the benzoic acid to which ferric chloride solution is added, and from which the precipitate produced is filtered off should show no violet coloration.

Sumatra Benzoic Acid; Cinnamic Acid.—1 g. of benzoic acid heated in a closed test tube in a boiling water-bath, with 1 g. of potassium permanganate and 10 c.c. of water for from ten to fifteen minutes, should give no smell of oil of bitter almonds on cooling.[1]

The British Pharmacopœia prescribes that benzoic acid should not develop the odour of benzaldehyde when warmed with its own weight of potassium permanganate, and ten times its weight of dilute sulphuric acid.

[1] *Cf.* also Schacht's reaction for Siamese benzoic acid ; *Merck's Reag.-Verz.,* 1908, p. 228.

Chemically prepared Acid.—1 g. of benzoic acid dissolves to a yellow or brown solution in 10 c.c. of ammonia, and the addition of excess of sulphuric acid causes the acid to separate out again. If to this mixture are added 5 c.c. of potassium permanganate solution (1 : 1000), the red colour of the latter should completely disappear after standing for four hours.

Hippuric Acid.—0·2 g. of benzoic acid are rubbed into a paste with a few drops of water and 0·3 g. of pure quicklime, then dried and ignited. No ammonia should be liberated.

Synthetic Benzoic Acid.—0·4 g. of benzoic acid is mixed with 0·6 g. of calcium carbonate free from chloride, and a little water, evaporated to dryness on the water-bath, and then ignited. On dissolving the residue in nitric acid and water, and making up to 20 c.c., the addition of silver nitrate solution should only produce a slight opalescence. This test, which shows the presence of chloro-benzoic acid, and which indicates whether chemically prepared benzoic acid from benzalchloride, benzyl-chloride, benzotrichloride, etc., has been added or not, is not absolutely reliable. Chemically pure benzoic acid comes into commerce containing no more chlorine than the acid sublimed from gum benzoin, and the addition of such a chemically pure acid to the acid from gum benzoin cannot be detected by the above reaction for chlorine. Only gross adulteration by means of cheap benzoic acid containing chlorine can be detected in this manner. This reaction has been retained up to now, since for a long time it was not possible to prepare the acid chemically, free or approximately free from chlorine.[1] H. Hagar,[2] in order to detect whether a benzoic acid is a pure product from sublimation or whether it has only been sublimed over gum benzoin, uses a reagent of doubtful value, prepared by acidifying a solution of ferric chloride and potassium ferricyanide with hydrochloric acid.

(b) Chemically pure Benzoic Acid.

This acid is distinguished from the acid obtained from gum benzoin by its pure white colour, its colourless solution in alcohol and ammonia, and its freedom from empyreumatic matter. It does not melt in boiling water, melts at 121°·4 and boils at 249°.

Tests for Impurities.

Inorganic and foreign Organic Matter.—1 g. of benzoic acid on heating should not leave more than 0·5 mg. of residue. Heated in a test tube it should sublime completely without charring. 1 g. of benzoic acid should dissolve in 20 c.c. of sulphuric acid to a colourless or only faint yellow solution.

[1] For the detection of chlorine in benzoic acid, cf. *Pharm. Zentralh.*, 1899, p. 183.

[2] *Pharm. Zentralh.*, **26**, 392.

Chloro-benzoic Acid.—0·4 g. of benzoic acid ignited with calcium carbonate and dissolved, as in the case with the official product, should show no immediate opalescence on the addition of silver nitrate solution, and on standing for five minutes only a faint turbidity.[1]

Quantitative Estimation.

The purity of benzoic acid may be controlled by titration with potassium hydroxide. For this purpose 1 g. of benzoic acid is dissolved in 10 c.c. of $N/1$ potassium hydroxide solution, diluted with 40 c.c. of water, and titrated with $N/1$ hydrochloric acid, using phenolphthalein as indicator. 1 c.c. of $N/1$ potassium hydroxide corresponds to 0·122048 g. of benzoic acid.

Bromoform.

$CHBr_3$.   Molec. wt. 252·77.

Bromoform is a colourless liquid with a smell somewhat similar to that of chloroform. It is very sparingly soluble in water, but is miscible in all proportions with alcohol, ether, benzene, and petroleum spirit. The purest bromoform has a sp. gr. of 2·904, melts at 9°, and boils at 149°-150°.

Tests for Impurities.

Non-volatile Matter.—20 c.c. of bromoform should leave no residue on volatilisation.

Bromine.—Bromoform should be quite colourless. On shaking 5 c.c. of bromoform with 5 c.c. of water, and 1 c.c. of zinc iodide-starch solution, the bromoform should remain colourless and the starch solution should not be immediately turned blue.

Hydrobromic Acid.—On shaking 10 c.c. of bromoform with 10 c.c. of water, the separated water should not immediately redden blue litmus paper. On carefully pouring the separated water on to silver nitrate solution, no opalescent ring should be visible at the point of contact of the two layers of liquid.

Foreign Organic Matter.—On shaking 10 c.c. of bromoform with 10 c.c. of sulphuric acid in a glass cylinder, previously washed out with sulphuric acid, the sulphuric acid should remain colourless for ten minutes.

Aldehyde.—On shaking 20 c.c. of bromoform with 10 c.c. of water, the separated water, on the addition of ammonia and silver nitrate solution, should show no reducing action on the silver nitrate for at least half an hour.[2]

[1] *Pharm. Zentralh.*, 1900, pp. 449, 529.
[2] On the decomposition of bromoform by light and air, cf. *Berichte der deutschen Pharm. Ges. Berlin*, 1905, p. 387 ; *J. Soc. Chem. Ind.*, 1906, **25**, 232.

Caffeine.

$$C_5HO_2N_4(CH_3)_3 + H_2O. \quad \text{Molec. wt. } 212 \cdot 14.$$
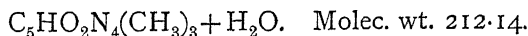
Caffeine crystallises in white, glistening, flexible needles which are soluble in 80 parts of water, 50 parts of alcohol (of about 85 per cent. by weight), and in 9 parts of chloroform; it is but sparingly soluble in ether. It effloresces in the air and loses its water of crystallisation completely at 100°. Melting point 235°.

An aqueous solution of caffeine is precipitated by tannic acid solution; the precipitate is soluble in an excess of the precipitating reagent. On evaporating a solution of 1 part of caffeine in 10 parts of chlorine water on the water-bath a yellowish-red residue remains, which changes to a beautiful purple-red colour on immediately treating with a little ammonia.[1]

Tests for Impurities.

Alkaloids.—Caffeine should dissolve to a colourless solution in concentrated sulphuric acid and in nitric acid. A cold, saturated solution of caffeine in water should not be rendered turbid by chlorine water or by iodine solution, and should remain colourless on the addition of ammonia.

Inorganic Impurities.—1 g. of caffeine should volatilise on heating without charring, and should not leave more than 0·5 g. of residue.

Caffeine is considerably more soluble in water in the presence of various salts such as sodium benzoate, sodium salicylate, and sodium cinnamate, than in water alone. This increased solubility is due to the formation of double salts; of these double salts caffeine-sodium salicylate and caffeine-sodium benzoate are the most important, and find application in pharmacy.

Caffeine-sodium Salicylate.

This double salt is prepared by evaporating a solution of 5 parts of caffeine and 6 parts of sodium salicylate in 20 parts of water. It is a white, amorphous powder or a white, granular mass containing 43·8 per cent. of caffeine, and is soluble in 2 parts of water and in 50 parts of alcohol (of about 85 per cent. by weight). On heating in a narrow test tube white vapours smelling of phenol are evolved, and the residue effervesces on treatment with acids. The aqueous solution even when very dilute (1 : 1000) gives a blue-violet coloration with ferric chloride. On warming the double salt with chloroform, the filtered liquid yields a crystalline residue on evaporation, which may be identified as caffeine.

[1] For identifying reactions, cf. *Merck's Reag.-Verz.*, 1908, p. 292.

Tests for Impurities.

An aqueous solution of caffeine-sodium salicylate (1 : 5) should be colourless. The double salt should dissolve in concentrated sulphuric acid without effervescence and to a colourless solution (sodium carbonate, sugar).

Heavy Metals and Sulphuric Acid.—The aqueous solution (1 : 20) should remain unchanged by sulphuretted hydrogen water and by barium nitrate solution.

Hydrochloric Acid.—2 c.c. of the solution (1 : 20), to which 3 c.c. of alcohol are added and then acidified with nitric acid, should not be affected by the addition of silver nitrate solution.

Water.—Caffeine-sodium salicylate should not lose more than 5 per cent. in weight on drying at 100°.

Quantitative Estimation of Caffeine.

A simple method of estimation consists in shaking up a solution of 1 g. of caffeine-sodium salicylate in 5 c.c. of water, four times successively, with about 5 c.c. of chloroform, evaporating off the chloroform, and weighing the residue after drying at 100°. At least 0·4 g. of caffeine should be found in the residue. By this method, the whole of the content of caffeine is not found, since a portion is retained in the aqueous solution.

Caffeine-sodium Benzoate.

Externally, this preparation does not differ from the preceding double salt. The caffeine can be extracted with chloroform, and gives, after evaporating off the solvent, the reactions given above. The aqueous solution gives a flesh-coloured precipitate with ferric chloride. Caffeine-sodium benzoate is prepared by evaporating down a solution of 5 parts of caffeine and 5 parts of sodium benzoate in 10 parts of water. The testing and quantitative estimation are carried out in exactly the same manner as given above for caffeine-sodium salicylate.

Camphor (Japan Camphor).

$C_{10}H_{16}O$. Molec. wt. 152·13.

Camphor comes into commerce in white, transparent, tough, crystalline masses. For pharmaceutical purposes it is sold in the form of balls, cubes, and also as " Flowers of Camphor." Crystallised from alcohol it forms hard hexagonal crystals. It has a peculiar smell and taste, and is difficultly soluble in water. According to the British Pharmacopœia the solubility is 1 : 700, according to Schmidt, 1 : 1200; it dissolves readily in alcohol, ether, chloroform, acetone, benzene, acetic acid, and carbon bisulphide, as well as in fatty and essential oils. Its

sp. gr. is 0·985-0·996, the melting point 175° (according to J. E. Crane and C. M. Joyce[1] 179°·4), and the boiling point 204°. It burns with a luminous, smoky flame. It is dextrorotatory in concentrated alcoholic solution, and its specific rotatory power according to Landolt is $(a)_D = +55·4$.

Tests for Impurities.

Non-volatile Matter.—On heating 1 g. of camphor, not more than 0·5 mg. of residue should remain.

"*Artificial*" *Camphor (Terpene hydrochloride).* — Japan camphor, when rubbed with an equal quantity of chloral hydrate, should give a syrupy liquid, whilst, according to Hirschsohn,[2] "artificial" camphor does not become liquid when treated in this manner.[3] Since "artificial" camphor contains chlorine it is readily identified. To test for its presence 0·5 g. of the sample is stirred into a molten mixture of potassium hydroxide and potassium nitrate, gently ignited, the cold melt dissolved in nitric acid and water, and the solution made up to 50 c.c.; on the addition of silver nitrate solution no turbidity should be produced.

Synthetic Camphor.—The synthetical preparation of camphor has made such advances in recent years that synthetic camphor has now become a commercial product. It has the same chemical composition as the natural product, but possesses different physical constants which serve for its identification. Natural camphor is dextrorotatory, gives on oxidation with nitric acid an optically active camphoric acid melting at 187°, and gives the Borisch reaction (see below). Synthetic camphor is optically inactive; on oxidation it yields an optically inactive acid melting at 202°-203°, and does not give the Borisch reaction. In dealing with a mixture of natural and synthetic camphor, the optical method is the only means of examination, the product to be examined being compared optically with a genuine sample of Japan camphor, both in solutions of equal concentration.

The alcoholic solution is most suitable for determining the specific rotatory power. For a solution in benzene Landolt and Förster give the following formula when using Laurent's apparatus at 20°:—

$$C = 115·205 \left[-1 + \sqrt{1 + \frac{0·04367 \cdot a}{l}} \right],$$

in which C = the weight of camphor in grams per 100 c.c. of solution, a = angle of rotation, and l = length of tube in decimetres.[4]

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[1] *J. Soc. Chem. Ind.*, 1907, **26**, 386.

[2] *Pharm. Zeit. f. Russland*, 1897, p. 161.

[3] *Cf.* also Bailey's and Dumont's reactions for artificial camphor. *Merck's Reag.-Verz.*, 1908, pp. 12 and 65.

[4] *Cf.* J. E. Crane and C. M. Joyce, *J. Soc. Chem. Ind.*, 1907, **26**, 386.

The Borisch Reaction.—On warming carefully 0·05 g. of camphor in a test tube with 1 c.c. of vanillin-hydrochloric acid, as the temperature gradually rises a rose-red coloration is first produced, which between 75°-100° changes to a greenish-blue. This reaction only takes place with natural camphor; synthetic camphor gives no coloration. The test may be carried out in the cold as follows:—About 0·1 g. of camphor is treated on a watch-glass with 10 drops of a cold mixture of equal volumes of vanillin-hydrochloric acid (1 g. of vanillin in 100 g. of 25 per cent. hydrochloric acid), and concentrated sulphuric acid added. A yellow coloration is at first produced, and in the course of half an hour to one hour in the case of natural camphor this changes to a dirty green coloration, and in the course of another hour to a pure dark green, and after seven to eight hours to an indigo-blue colour. (Impurities in natural camphor mask the reaction.) Synthetic camphor treated in a similar manner only shows the initial yellow coloration, which disappears at the end of an hour.[1]

The oxidation of camphor is carried out as follows:—5 g. of camphor are placed in a small flask fitted with a long vertical glass tube or upright Liebig's condenser, and heated on the boiling water-bath for about fifty hours with a mixture consisting of 24 c.c. of nitric acid (sp. gr. 1·42) and 16 c.c. of water. The camphoric acid which has separated is then collected, washed with cold water, recrystallised from hot water, converted into the sodium salt, again separated by the addition of hydrochloric acid and recrystallised several times from hot water. As stated above, natural camphor yields by this treatment an acid melting at 187°, whilst synthetic camphor yields an acid melting at 202°-203°, or, as is frequently the case, no acid at all, owing to the oxidation having proceeded too rapidly.[2]

Carbon Bisulphide.

CS_2. Molec. wt. 76·14.

Carbon bisulphide is a colourless, bright, neutral, highly refractive, easily inflammable liquid, having a sp. gr. of 1·270-1·272, and a boiling point of 46°-47°.

Tests for Impurities.

Pure carbon bisulphide contains generally only sulphur as an impurity, which is found in traces in practically all of the purest commercial brands. On evaporating 50 c.c. of carbon bisulphide on

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[1] *Pharm. Zentralh.*, 1907, **48**, 527 and 777 ; *J. Soc. Chem. Ind.*, 1907, **26**, 1065.

[2] *Cf.* Deussen, *Arch. Pharm.*, 1909, **247**, 311. On testing synthetic camphor, *cf.* A. Baselli, *J. Soc. Chem. Ind.*, 1907, **26**, 431.

the water-bath, only a trace of sulphur should remain. On shaking carbon bisulphide with lead carbonate, the latter should not be turned brown (absence of sulphuretted hydrogen).

Sulphuric and Sulphurous Acids.—On shaking 10 c.c. of carbon bisulphide with 5 c.c. of water, the latter should neither redden nor bleach blue litmus paper.

Quantitative Estimation.

A quantitative estimation of carbon bisulphide is usually not necessary if the sample conforms to the tests given above. If, however, a quantitative valuation be required, the method based on A. W. Hofmann's xanthate reaction may be used.[1] A weighed quantity of carbon bisulphide is added to alcoholic potassium hydroxide, and after allowing to react for a short time the mixture is acidified with acetic acid and insoluble cuprous xanthate (a yellow crystalline precipitate) precipitated by the addition of copper sulphate. The contained copper may be estimated either volumetrically according to Grete,[2] and Macagno,[3] or weighed as cupric oxide. From the weight of copper found the value of the carbon bisulphide may be calculated, since one equivalent of copper corresponds to two equivalents of carbon bisulphide.[4]

Carbon Tetrachloride.

CCl_4. Molec. wt. 153.84.

Carbon tetrachloride is a colourless liquid, sparingly soluble in water (about 0.08 to 100), miscible in all proportions with absolute alcohol, ether, fatty and essential oils. Its sp. gr. is 1.604, and its boiling point 76°-77°.

Tests for Impurities.

Non-volatile Matter.—On evaporating 25 c.c. of carbon tetrachloride on the water-bath, no appreciable residue should be left.

Chlorine.—No blue coloration should be produced on shaking 20 c.c. of carbon tetrachloride with 5 c.c. of zinc iodide-starch solution.

Hydrochloric Acid.—20 c.c. of carbon tetrachloride are shaken with 10 c.c. of water for about one minute. The separated water should not react acid and should show no reaction with silver nitrate solution.

Organic Impurities.—On shaking 20 c.c. of carbon tetrachloride frequently during one hour with 15 c.c. of concentrated sulphuric acid in

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[1] *Cf.* section on "Coal Tar," Vol. II., Part II., p. 796.
[2] *Z. anal. Chem.*, 1882, **21**, 133.   [3] *Ibid.*
[4] *Cf.* A. Goldberg, *Z. angew. Chem.*, 1899, **12**, 75; *J. Soc. Chem. Ind.*, 1889, **18**, 304.

a stoppered glass vessel, previously rinsed out with sulphuric acid, the sulphuric acid should not become coloured.

Aldehyde.—If a mixture of 10 c.c. of carbon tetrachloride and 10 c.c. of potassium hydroxide solution (1·3) be warmed for about one minute and frequently shaken during the warming, the potassium hydroxide should not become either yellow or brown in colour.

Carbon Bisulphide.—10 c.c. of carbon tetrachloride are mixed with 10 c.c. of a solution of 10 g. of potassium hydroxide in 100 c.c. of absolute alcohol. After standing for one hour, 5 c.c. of dilute acetic acid (sp. gr. 1·04-1·042) and copper sulphate solution are added. No yellow precipitate should separate within two hours.

Any carbon bisulphide present may be quantitatively determined by the iodometric method worked out by L. G. Radcliffe,[1] as an applicable modification of Gastine's form of the xanthate reaction. The method is based on the conversion of the carbon bisulphide into xanthic acid by means of alcoholic potash, separating it by the addition of acetic acid, and titrating with iodine solution, whereby it is oxidised to ethyl dithio-dicarbonate. To carry out the determination, 25 c.c. of alcoholic potash are run into a flask of suitable size, and the flask loosely closed with a cork and tared; 1 c.c. of the carbon tetrachloride under examination is then run in from a pipette and the total weight accurately determined. After five minutes, dilute acetic acid is added until the mixture reacts faintly acid (discoloration of phenolphthalein), the contents of the flask cooled, and solid sodium bicarbonate added in excess. The milky, turbid mixture is titrated with $N/10$ iodine solution after the addition of starch solution. One molecule of xanthic acid corresponds to one atom of iodine, as shown in the following equation:—

$$2CS{<}{\substack{OC_2H_5 \\ SH}} + I_2 = S_2(CS.OC_2H_5)_2 + 2HI.$$

Xanthic acid   Ethyl dithio-dicarbonate
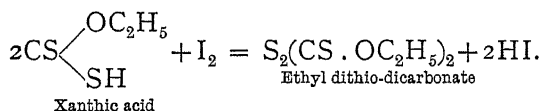
Casein.

Casein, an albuminoid constituent of milk, is a fine, white or yellowish-white powder, insoluble in water and in alcohol. Sprinkled on moist blue litmus paper, the latter is turned red. It is soluble in aqueous solutions of the alkali hydroxides and alkaline earths, as well as in alkaline carbonates, and is precipitated out from these solutions by acids. Excess of alkali converts it into albuminate. On artificial digestion in 0·2 per cent. hydrochloric acid with pepsin at about 40°, the clear solution of casein gradually becomes turbid owing to the separation of nuclein.

[1] *J. Soc. Chem. Ind.*, 1909, **28**, 229.

According to Scherer[1] and O. Hammarsten[2] the elementary composition of casein is as follows:—

	Scherer. Per cent.	Hammarsten. Per cent.
Carbon .	54·02	52·96
Hydrogen	7·33	7·05
Nitrogen	15·52	15·65
Sulphur .	0·75	0·71
Phosphorus	...	0·85
Oxygen .	22·38	22·78

Phosphorus is a constituent of casein itself, though it was formerly assumed to be only a constituent of the contained mineral matter left on ignition.

Tests for Impurities.

Inorganic Matter.—On burning 1 g. of casein in free access of air, only a trace of ash should remain behind. The purest casein yields up to 0·5 per cent. of ash (according to Hammarsten up to 1·2 per cent.), commercial casein as much as 6 per cent., and the purest casein from plants up to 1 per cent. In judging casein, these figures for the percentage of ash may generally be considered as the maxima. Sodium casein sometimes comes on to the market under the designation of casein. The salt is readily recognised by its solubility in water and high percentage of ash (sodium carbonate).

Fat.—10 g. of casein are well shaken frequently for one hour with 100 c.c. of ether, 50 c.c. of the ethereal extract filtered through a dry filter paper into a small weighed flask, well covering the funnel to avoid loss of ether by evaporation, and the ether evaporated off on the water-bath. The residue is then dried for two hours at 90°-100° and weighed. Good casein should not contain more than 0·1 per cent. of fat. In the purest casein up to 0·07 per cent., in commercial casein up to 0·09 per cent., and in casein from plants up to 0·01 per cent. of fat will be found.

Free Acid (Acetic Acid).—The purest casein should contain no free acid, which, however, is frequently not the case with commercial products. On shaking 10 g. of casein with 100 c.c. of water, the filtrate should react only slightly acid; 50 c.c. of the filtrate may be titrated with $N/10$ potassium hydroxide, using phenolphthalein as indicator. A good sample should not require more than 0·5 c.c. of the $N/10$ potassium hydroxide to produce a red coloration.

Quantitative Estimation.

This may be carried out by determining the content of nitrogen either by Dumas' or Kjeldahl's method. Taking the nitrogen con-

[1] *Annalen*, 1841, 40, 41.
[2] *Z. physiol. Chem.*, 1882-3, 7, 269; cf. also Tangl, *Pflüger's Archiv der Physiol.*, 1908, 121, 534.

tent of milk albumin as 14·3 per cent., the calculation used in the analysis of casein is to multiply the percentage of nitrogen found in the sample under examination by 6·99. A good sample of casein is expected to give a value of 100 when multiplied by this factor.

According to H. D. Richmond[1] the Kjeldahl method is better and more reliable than the Dumas method for the estimation of nitrogen in casein. Experimental results gave a mean value of 15·65 per cent. of nitrogen in casein, corresponding to the factor 6·39.

Catechol (Pyrocatechin).

$$C_6H_4 \begin{cases} OH(1) \\ OH(2) \end{cases}. \quad \text{Molec. wt. } 110·05.$$
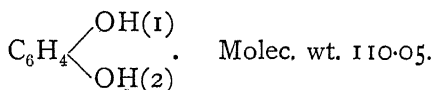
Catechol forms colourless, glistening, slightly odourous, rhombic scales or columnar crystals, readily soluble in ether, alcohol, benzene, chloroform, and water. The aqueous solution reacts acid. It melts at 104°, and boils at 240°-245°.

An aqueous solution of catechol gives a green coloration with ferric chloride; on the addition of a little sodium hydroxide the colour changes to violet, and with excess to deep red. Silver nitrate is reduced by catechol in the cold, but Fehling solution is only reduced on heating. The aqueous solution is precipitated by lead acetate as well as by the basic acetate. This differentiates catechol from resorcinol and quinol; resorcinol in aqueous solution is precipitated by basic lead acetate, but not by the normal acetate, whilst quinol is precipitated by neither of these reagents.[2]

Tests for Impurities.

Inorganic Matter.—1 g. of catechol should not leave more than 0·5 mg. of residue on ignition.

Phenol.—On boiling an aqueous solution (1:10) it should not be possible to recognise the smell of phenol.

Foreign Organic Matter.—Catechol dissolves in sulphuric acid producing a faint rose coloration; no darkening of the sulphuric acid should take place.

Quantitative Estimation.

0·5 g. of catechol is dissolved in 50 c.c. of water and a concentrated aqueous solution of lead acetate gradually run in, the contents of the beaker being kept agitated during the addition. After allowing the white precipitate ($C_6H_4O_2Pb$) to settle, a few more drops of lead acetate

[1] *Analyst*, 1908, **33**, 179.
[2] For colour reactions, cf. *Chem. Zentr.*, 1898, II., 1282 ; *Z. anal. Chem.*, 1889, **28**, 252, and 1895, **34**, 235.

solution are added in order to see if the precipitation is complete, and the precipitate is then collected on a weighed filter paper. After washing several times with water, the precipitate is dried at 100° and weighed. The result obtained may be checked by igniting the precipitate, dissolving in nitric acid, diluting the solution with water, precipitating the lead as sulphate and weighing it as such.

1 g. $PbC_6H_4O_2$ corresponds to 0.3494 g. of catechol; 1 g. of lead sulphate corresponds to 0.3632 g. of catechol.

Chloral Hydrate.

$CCl_3COH . H_2O$. Molec. wt. 165.40.

Chloral hydrate forms colourless, transparent, monoclinic crystals, which soften at 49° and melt at 53°. It dissolves readily in water, alcohol, and in ether, but only sparingly and slowly in benzene, chloroform, petroleum spirit, and carbon bisulphide. In aqueous solution it reacts slightly acid, whilst in other solvents it has a neutral reaction.

On treating chloral hydrate with potassium hydroxide solution, chloroform is produced.[1] The following test serves to differentiate between chloral hydrate and butyl-chloral hydrate :—On treating chloral hydrate with a solution of pyrogallol in concentrated sulphuric acid, the mixture remains colourless in the cold, but on warming carefully and gently a fine blue coloration is produced; butyl-chloral hydrate treated in a similar manner yields a wine-red coloration.[2]

Tests for Impurities.

Inorganic Matter.—1 g. of chloral hydrate should leave no appreciable residue on ignition.

Hydrochloric Acid.—An alcoholic solution of chloral hydrate (1 : 10) should not show any immediate turbidity with silver nitrate solution, and should not redden blue litmus paper.

Chloral Alcoholate.—On pouring 1 c.c. of commercial nitric acid over 1 g. of chloral hydrate in a porcelain dish, no yellow coloration should be produced at the ordinary temperature, or on warming for from three to four minutes on the water-bath, and also no yellow vapours should be evolved even on warming for ten minutes. The British Pharmacopœia gives the following test:—When 1 g. of chloral hydrate is warmed with 6 c.c. of water and 0.5 c.c. of potassium hydroxide solution, the mixture filtered, sufficient iodine solution added to impart a deep brown colour, and the whole set aside for an hour, no precipitate of iodoform should result.

[1] For identifying and colour reactions of chloral hydrate, cf. *Merck's Reag.-Verz.*, 1908, p. 292.

[2] *Pharm. Zeit.*, 1904, p. 91.

Foreign Organic Matter.—1 g. of chloral hydrate when shaken up with 10 c.c. of sulphuric acid in a glass vessel previously rinsed out with sulphuric acid should not discolour the acid within one hour. Chloral hydrate required for medicinal purposes should conform to the following more exacting test :—If 2 g. of chloral hydrate are dissolved in 10 c c. of sulphuric acid (sp. gr. 1·84) in a glass-stoppered flask previously rinsed out with sulphuric acid, and 4 drops of formaldehyde (40 per cent.) added, the mixture should not become discoloured within half an hour.[1]

Quantitative Estimation.

Potassium hydroxide, even in the cold, decomposes chloral hydrate quantitatively into chloroform and potassium formate :—

$$CCl_3COH \cdot H_2O + KOH = CHCl_3 + H \cdot COOK + H_2O.$$
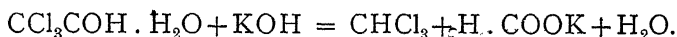
To carry out the estimation based on this decomposition 5 g. of chloral hydrate are dissolved in 50 c.c. of $N/1$ potassium hydroxide, phenolphthalein added, and the excess of alkali immediately titrated with $N/1$ hydrochloric acid. In order to arrive at the content of chloral hydrate in the 5 g. of the sample taken, the number of cubic centimetres of $N/1$ potassium hydroxide used for the reaction is multiplied by 0·1654. Should the chloral hydrate contain free hydrochloric acid, 10 g. of the sample are treated in a 100 c.c. measuring flask with 0·5 g. of calcium carbonate and 50 c.c. of water, and the mixture well shaken for some minutes. The flask is then filled up to the mark with water, the contents well mixed and filtered, and 50 c.c. of the filtrate are then treated with 50 c.c. of $N/1$ potassium hydroxide, as given above.

T. E. Wallis[2] gives the following method :—0·1 g. of chloral hydrate is dissolved in 10 c.c. of alcohol, 10 c.c. of $N/1$ sodium hydroxide added, and the mixture heated in a suitable bottle, closed with a rubber cork which is securely tied down, for three hours in the water-bath. The resulting mixture is neutralised with $N/1$ sulphuric acid, using phenolphthalein as indicator, and the sodium chloride formed in the reaction titrated with $N/10$ silver nitrate solution. The calculation is made according to the following equation :—

$$CCl_3CH(OH)_2 + 5NaOH = 3NaCl + 2H \cdot COONa + 3H_2O.$$
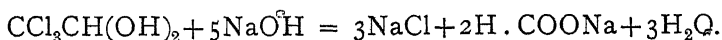
Not less than 18·1 and not more than 18·3 c.c. of $N/10$ silver nitrate solution should be required.

The estimation of the contained chlorine is also made use of in the method of valuation devised by P. A. W. Self.[3] This consists in heating 0·3 g. of chloral hydrate with 1·0 g. of aluminium powder (or 2·5 g.

[1] *Merck's Jahresber.*, 1910, p. 150.   [2] *Pharm. J.*, 1906, **76**, 162.
[3] *Ibid.*, 1907, **79**, 4.

of zinc filings), 15 c.c. of glacial acetic acid, and 40 c.c. of water for half an hour under a reflux condenser. The mixture is then filtered, and, after washing, the chlorine in the solution is determined either gravimetrically as silver chloride, or volumetrically by adding excess of $N/10$ silver nitrate solution, filtering, and titrating the excess of silver with ammonium thiocyanate.

E. Rupp[1] gives the following iodometric method of estimation :—25 c.c. of $N/10$ iodine solution and 2·5 c.c. of $N/1$ potassium hydroxide solution are run into a glass-stoppered flask. 10 c.c. of a 1 per cent. chloral hydrate solution are added to the above mixture, and the contents of the flask allowed to stand for from five to ten minutes. After diluting with about 50 c.c. of water and adding 5 c.c. of hydrochloric acid (25 per cent.), the solution is titrated with $N/10$ sodium thiosulphate solution. From 12·9-13·5 c.c. should be required, which correspond to 100-95 per cent. of chloral hydrate. The decomposition takes place according to the following equation :—

$$CCl_3CH(OH)_2 + I_2 = 2HI + CO_2 + CHCl_3.$$
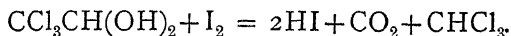
1 c.c. of the iodine solution is therefore equal to 0·00827 g. of chloral hydrate.

Chloroform.

CHCl$_3$. Molec. wt. 119·39.

Chloroform is a clear, colourless liquid, possessing a characteristic smell. The purest chloroform has a sp. gr. of 1·502, and boils at 62°; C. Baskerville and W. Hamor give the boiling point of specially purified chloroform as 61°·2, and the sp. gr. at 15°/4° as 1·49887.[2] The chloroform of the British Pharmacopœia is prepared by the addition of sufficient absolute alcohol to produce a liquid having a sp. gr. of not less than 1·490 and not more than 1·495. That of the German Pharmacopœia contains an addition of 1 per cent. of alcohol and has a sp. gr. of from 1·485-1·489, and boils between 60°-62°. The addition of alcohol makes the preparation more stable.[3]

Chloroform is only slightly soluble in water (1 : 200); it is miscible in all proportions with alcohol, ether, carbon bisulphide, fatty and essential oils. On warming chloroform with potassium hydroxide and acetanilide, the disagreeable odour of isonitrile is produced.

Tests for Impurities.

Inorganic and non-volatile Organic Matter.—On evaporating 25 c.c. of chloroform, no appreciable residue should be left.

[1] *Arch. Pharm.,* 1903, 241, 326 ; *J. Soc. Chem. Ind.,* 1903, 22, 1019.

[2] *J. Ind. Eng. Chem.,* 1912, 4, 212 ; *J. Soc. Chem. Ind.,* 1912, 31, 840.

[3] On the value of alcohol for increasing the stability of chloroform, *cf.* Adrian, *J. Pharm. Chim.,* 1903, 18, 5 ; *J. Soc. Chem. Ind.,* 1903, 22, 879.

Hydrochloric Acid.—On shaking 20 c.c. of chloroform with 10 c.c. of water for about a minute, the separated water should not redden blue litmus paper, and when poured on to silver nitrate solution the line of separation of the two layers of liquid should show no turbidity.[1]

Chlorine.—On shaking 20 c.c. of chloroform with 5 c.c. of zinc iodide-starch solution, the chloroform should not become coloured nor the starch solution turned blue.

Foreign Organic Matter.—20 c.c. of chloroform, 15 c.c. of concentrated sulphuric acid, and 4 drops of formaldehyde solution (40 per cent.) are shaken together in a glass-stoppered flask previously rinsed out with sulphuric acid; the sulphuric acid should not become discoloured within half an hour.[2]

Carbonyl Chloride.—The smell of chloroform should not be irritating. 20 c.c. of chloroform are treated with a solution of 3 drops of aniline in 5 c.c. of benzene. In the presence of carbonyl chloride either a turbidity or a crystalline precipitate of phenyl urea is produced.[3] On adding clear baryta water to 10 c.c. of chloroform, no white film should be produced at the junction of the two layers of liquid.

Alcohol.—Chloroform free from alcohol should not discolour potassium permanganate solution. According to H. Hager, a somewhat high content of alcohol may be detected by shaking up chloroform with a mixture of 4 vols. of glycerol and 1 vol. of water in a graduated cylinder. The content of alcohol can be gravimetrically estimated by a method given by M. Nicloux.[4]

Aldehyde.—If 10 c.c. of chloroform and 10 c.c. of potassium hydroxide solution are warmed together for about a minute, no yellow or brown coloration should result.

The following scheme for the examination of chloroform for anæsthetic and analytical purposes, with particular reference to the detection of avoidable impurities, has been worked out by C. Baskerville and W. Hamor, as the result of an extended investigation of the subject.[5] " Anæsthetic chloroform " is the term given to chloroform complying with pharmacopœial requirements; it contains ethyl alcohol (up to 1 per cent.) and small quantities of water. " Commercial chloroform " contains at least 99 per cent., by weight, of chloroform, but may contain small amounts of " organic impurities."

1. *Specific gravity* is determined by means of a pyknometer at 15°.

[1] On the decomposition of chloroform by air and light, cf. W. Ramsay, *J. Soc. Chem. Ind.*, 1892, 11, 772 ; also, *Ber. der deutsch. pharm. Ges. Berlin*, 1905, p. 387, and C. Baskerville and W. Hamor, *J. Soc. Chem. Ind.*, 1912, 31, 840.

[2] On the preservation of chloroform for anæsthetic purposes, cf. *Merck's Jahresber.*, 1902, p. 43 ; also, *Z. angew. Chem.*, 1910, 23, 1546.

[3] Scholvien, *Pharm. Zentralh.*, 34, 611:

[4] *Bull. Soc. Chim.*, 1906, 35 330 ; *J. Soc. Chem. Ind.*, 1906, 25, 611.

[5] *J. Ind. Eng. Chem.*, 1912, 4, 212, 278, 362, 422, 499, 571 ; *J. Soc. Chem. Ind.*, 1912, 31, 839.

2. *Odour.*—100 c.c. are slowly evaporated to about 10 c.c. on the water-bath. The residue from anæsthetic chloroform should be colourless and possess no foreign odour, and when allowed to evaporate on filter paper, no odour of other substances than alcohol and chloroform should be perceptible as the last portions disappear. (In the case of pure chloroform, no odour except that of chloroform should be observed.)

3. *Residue.*—No appreciable residue should be left when 100 c.c. of pure or anæsthetic chloroform are evaporated in a platinum dish at 100°.

4. *Organic Impurities.*—20 c.c. of the sample are mixed with 15 c.c. of concentrated sulphuric acid in a glass-stoppered tube of 50 c.c. capacity, and after the addition of 0·4 c.c. of pure 40 per cent. formaldehyde solution, the whole is shaken for five minutes. No coloration should be produced with anæsthetic chloroform, and with pure chloroform no coloration should be produced even on allowing to stand for one hour in the dark.

5. *Water.*—When 20 c.c. of the sample are boiled with 1 g. of clean crystals of calcium carbide, and the vapours evolved passed into ammoniacal silver nitrate solution, no acetylene reaction should result in the case of pure chloroform or anhydrous anæsthetic chloroform.[1] In the case of anæsthetic chloroform, 10 c.c. should dissolve to a clear solution when shaken with an equal volume of paraffin oil of sp. gr. 0·880.

6. *Alcohol.*—For pure chloroform, 10 c.c. are extracted with successive portions of 4 c.c., 4 c.c., and 2 c.c. of concentrated sulphuric acid, the acid solution is diluted with 40 c.c. of water, and gently distilled until 20 c.c. have passed over. 10 c.c. of the distillate are treated with 6 drops of a 10 per cent. solution of potassium hydroxide, warmed to 50°, and treated with a saturated solution of iodine in potassium iodide until it becomes permanently brown, when it is carefully decolorised with potassium hydroxide; no iodoform should be deposited. A negative result with this test indicates the absence of alcohol, acetaldehyde, propyl alcohol, acetone, etc. Tests with chromic acid,[2] alkaline permanganate,[3] and potassium hydroxide (agitation of the sample first with ignited potassium carbonate to remove water, and then with a small piece of fused potassium hydroxide and red litmus paper; the latter becomes blue in presence of alcohol) may be used for ·confirmatory purposes. In the case of anæsthetic chloroform and commercial chloroform, the amount of alcohol present should be determined by the method of Nicloux[4] as modified by the authors (shaking the chloroform for at least ten times in succession with twice its volume of water and using a

[1] Cf. *J. Soc. Chem. Ind.*, 1898, **17**, 864.　　　[2] Cf. *Ibid.*, 1896, **15**, 748.
[3] Cf. *Ibid.*, 1882, **I**, 117.　　　[4] Cf. *Ibid.*, 1906, **25**, 611.

portion of the combined aqueous extracts for the determination), or by Behal and François' method.[1]

7. *Acetone.*—For pure chloroform see (6). For anæsthetic chloroform 10 c.c. are agitated with 5 drops of a 0·5 per cent. solution of sodium nitroprusside and 2 c.c. of ammonia of sp. gr. 0·925, and the mixture allowed to stand for several minutes. When acetone is present, the supernatant liquid acquires an amethyst colour. The test should also be applied to the first 10 per cent. of distillate and the 10 per cent. of residue obtained on slowly distilling 100 c.c. of the sample. If the proportion of acetone is as low as 1 : 1000, the amethyst colour is not distinct until the mixture of chloroform with ammonia and sodium nitroprusside is saturated with ammonium sulphate, shaken, and then allowed to stand for five minutes. In all cases a blank test should be made with pure chloroform for comparison.

8. *Acetaldehyde.*—With chloroform of all grades, no coloration should be produced even after fifteen minutes when 5 c.c. are agitated with 5 c.c. of François' reagent (22 c.c. of sulphurous acid, 30 c.c. of 1 : 1000 rosaniline acetate solution, and 3 c.c. of sulphuric acid). For pure chloroform, in addition to test (6), no coloration should be produced when 5 c.c. are shaken with 5 c.c. of Nessler's reagent and the mixture allowed to stand for five minutes. For anæsthetic chloroform, 10 c.c. are shaken with 10 c.c. of water and 5 drops of Nessler's reagent, and the mixture allowed to stand for five minutes; no precipitate should be produced, and the reagent should not become coloured, although it may become opalescent or slightly turbid.

9. *Acidity.*—20 c.c. of the sample are thoroughly agitated with 10 c.c. of water and 2 drops of phenolphthalein solution, and then titrated with $N/100$ potassium hydroxide solution ; in the case of either pure or anæsthetic chloroform, not more than 0·2 c.c. of the alkali solution should be required to produce a faint but decided alkaline reaction permanent for fifteen minutes, when the mixture is shaken for thirty seconds after the addition of each drop of alkali.

10. *Decomposition Products of Pure Chloroform.*—A dry stoppered tube of 25 c.c. capacity, containing 15 c.c. of the sample, is filled with a clear solution of barium hydroxide (1 : 19) and allowed to stand for three hours in the dark, without agitation ; the formation of a film of barium carbonate indicates the presence of carbonyl chloride. In addition to test (9), both pure and anæsthetic chloroform should comply with the following test :—When 10 c.c. are agitated with 5 c.c. of water for five minutes, the aqueous extract should not become turbid or give any precipitate on addition of silver nitrate solution (absence of hydrochloric acid, chlorides, etc.), and no reduction should occur on warming (absence of acetaldehyde, formic acid and formates, etc.). With chloroform of all

[1] Cf. *J. Soc. Chem. Ind.*, 1897, **16**, 566.

grades, no liberation of iodine, as indicated by addition of starch solution, should result when 10 c.c. are shaken during fifteen minutes with 10 c.c. of a 10 per cent. solution of cadmium potassium iodide (absence of chlorine and hydrogen peroxide).

11. *Decomposition Products of Anæsthetic Chloroform.*—For the detection of acetaldehyde see (8). If the sample fails to comply with test (9) and contains none of the impurities referred to under (10), the presence of acetic acid is indicated, and the sample should be rejected. For the detection of chlorinated derivatives of the oxidation products of alcohol, 20 c.c. of the sample are shaken during twenty minutes with 15 c.c. of concentrated sulphuric acid, and 2 c.c. of the mixture are diluted with 5 c.c. of water; the liquid should remain colourless and clear, and should possess no odour foreign to anæsthetic chloroform (chloroform and alcohol); it should remain colourless when further diluted with 10 c.c. of water, and its transparency should not be diminished on addition of 5 drops of silver nitrate solution.

Quantitative Estimation.

Chloroform may be estimated either volumetrically by the method given by L. de Saint-Martin,[1] or iodometrically according to the method due to G. Vortmann.[2]

Cinnamic Acid.

$C_6H_5 . CH : CH . COOH.$ Molec. wt. 148·06.

Cinnamic acid crystallises in colourless, odourless needles or rhombic prisms which melt at 133° and boil at 300° with partial decomposition. It dissolves in about 3500 parts of cold water, more readily in boiling water, in 4·5 parts of alcohol, in 17 parts of chloroform, and in 110 parts of carbon bisulphide. On warming 0·1 g. of cinnamic acid in the water-bath with 20 c.c. of potassium permanganate solution (1 : 1000), a smell of benzaldehyde is produced.

Tests for Impurities.

Inorganic Matter.—On igniting 1 g. of cinnamic acid not more than 0·5 mg. of residue should remain.

Sulphuric and Hydrochloric Acids.—Neither barium nitrate nor silver nitrate solutions should show any reaction with a solution of 1 g. of cinnamic acid in 25 c.c. of boiling water.

Foreign Organic or Resinous Matter.—On dissolving 1 g. of cinnamic acid in hot sulphuric acid, at most only a light yellow coloration and not a brown coloration should result.

Benzoic Acid.—On thoroughly shaking 1 g. of cinnamic acid with

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[1] *Comptes rend.*, 1888, **106**, 492.; *J. Chem. Soc. Abstr.*, 1888, **54**, 570.

[2] *Anleitung zur chemischen Analyse organischer Stoffe*, 1891, pp. 102 and 401.

100 c.c. of water at 20° at intervals during one hour, and filtering, 50 c.c. of the filtrate should not require more than 1·4 c.c. of $N/10$ sodium hydroxide for neutralisation, using phenolphthalein as indicator. At 20°, cinnamic acid is soluble to the extent of 1 : 2400, and benzoic acid of 1 : 360. Treated as above, benzoic acid yields a filtrate, 50 c.c. of which require 11·2 c.c. of $N/10$ sodium hydroxide for neutralisation. Traces of benzoic acid in cinnamic acid cannot be detected by this method, which only detects quantities over 1 per cent.

A sample containing 1 per cent. of benzoic acid, treated as above, requires 1·6 c.c. of $N/10$ sodium hydroxide for neutralisation. According to A. W. de Jong[1] the benzoic acid in cinnamic acid may be determined by converting the cinnamic acid into phenyldibromopropionic acid, which does not volatilise at 100°. The mixture of the two acids (about 2 g.) in carbon bisulphide is treated with bromine, and after allowing to stand for twenty-four hours the carbon bisulphide and excess of bromine are distilled off; the residue is taken up with ether, the ethereal solution evaporated at the ordinary temperature, the residue dried *in vacuo* over sulphuric acid, then powdered and heated to 100°. The residual phenyldibromopropionic acid is weighed, and the content of benzoic acid thus obtained by difference. By determining the bromine in the residual substance and the quantity of sublimed benzoic acid, the presence of other substances in the mixture can be detected.

Quantitative Estimation.

1 g. of cinnamic acid is dissolved in 10 c.c. of $N/1$ sodium hydroxide and some water, and titrated with $N/1$ hydrochloric acid, using phenolphthalein as indicator. 1 c.c. of sodium hydroxide neutralised corresponds to 0·1481 g. of cinnamic acid.

Citric Acid.[2]

$$C_6H_8O_7 + H_2O. \text{Molec. wt. } 210·08.$$

Citric acid crystallises in large, colourless, rhombic prisms, which do not effloresce in dry air at the ordinary temperature, but which lose their water of crystallisation completely at 100° ; in a damp atmosphere the crystals become moist superficially. The crystallised acid has no fixed melting point, since it fuses together at 70°-75°, but the anhydrous acid melts at 153°-154°. Citric acid dissolves in 0·75 parts of cold water, in 0·5 parts of boiling water, in 1 part of alcohol (about 85 per cent.), and in about 50 parts of ether. On dissolving

[1] *Rec. trav. chim.*, 1909, **28**, 342 ; 1911, **20**, 223 ; *J. Soc. Chem. Ind.*, 1910, **29**, 112 ; 1911, **30**, 1407.
[2] *Cf.* the section on "Citric Acid," this Vol., pp. 296 *et seq.*

0·1 g. of the acid in 1 c.c. of water and adding 40-50 c.c. of lime water, (the solution must react alkaline), a white flocculent precipitate is formed on boiling; on cooling the solution, the precipitate redissolves within three hours.

Tests for Impurities.

Inorganic Matter.—1 g. of citric acid should leave no appreciable residue on ignition.

Calcium Citrate.—No precipitate should be produced on adding ammonium oxalate solution to 20 c.c. of an aqueous solution of the acid (1 : 10) containing excess of ammonia.

Lead; Copper; Iron.—A solution of 5 g. of citric acid in 10 c.c. of water, nearly neutralised with ammonia so that the solution only reacts faintly acid (12 c.c. of sp. gr. 0·96), should remain unchanged on treatment with sulphuretted hydrogen.

Sulphuric Acid.—20 c.c. of an aqueous solution of citric acid (1 : 10) should give no turbidity with barium chloride solution.

Sugar; Tartaric Acid; Oxalic Acid.—A mixture of 1 g. of citric acid and 10 c.c. of sulphuric acid, prepared in a porcelain mortar previously cleaned with sulphuric acid, when heated in a test tube in a boiling water-bath for one hour, should not darken and at most only turn yellow.

1 g. of citric acid dissolved in 2 c.c. of water should not become turbid on the addition of 10 drops of potassium acetate solution and 5 c.c. of alcohol, and on standing for two hours no crystalline precipitate should separate.[1]

Quantitative Estimation.

1 g. of crystallised citric acid (with $1 H_2O$) requires 14·3 c.c. of $N/1$ potassium hydroxide for neutralisation. 1 c.c. of $N/1$ potassium hydroxide corresponds to 0·07003 g. of citric acid. Phenolphthalein is used as indicator.

Cocaine Hydrochloride.

$$C_{17}H_{21}O_4N . HCl. \quad \text{Molec. wt. 339·65.}$$
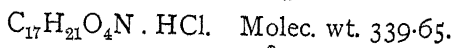
Cocaine hydrochloride forms colourless, prismatic crystals which decompose on melting at 183°. It is readily soluble in water and in alcohol. Applied to the tongue, solutions of cocaine hydrochloride produce temporary insensibility. On heating 1 g. of cocaine hydrochloride to about 100° for five to ten minutes with 10 c.c. of sulphuric acid, and carefully mixing the resulting product with 20 c.c. of water,

[1] For reactions for the detection of tartaric acid in citric acid, *cf.* also *Merck's Reag.-Verz.*, 1908, p. 302.

the smell of methyl benzoate may be recognised and a considerable separation of benzoic acid occurs. On treating an aqueous solution of cocaine hydrochloride with a few drops of nitric acid and silver nitrate solution, a white precipitate of silver chloride is produced.[1]

Tests for Impurities.

Inorganic Matter.—On igniting 0·5 g. of cocaine hydrochloride not more than 0·5 mg. of residue should remain.

Free Hydrochloric Acid.—An aqueous solution of cocaine hydrochloride should react neutral.

Cinnamyl Cocaine and Organic Impurities.—According to the British Pharmacopœia a solution containing not less than 1 per cent. of cocaine gives a copious red precipitate with an excess of a solution of potassium permanganate which should not change colour within an hour. The German Pharmacopœia prescribes the following test :— A solution of 0·1 g. of cocaine hydrochloride in 5 c.c. of water and 3 drops of dilute sulphuric acid should assume a violet coloration on the addition of 5 drops of potassium permanganate solution (1 : 1000). In the absence of dust, the coloration should show but little signs of fading in the course of half an hour.

Perfectly pure cocaine hydrochloride conforms to the following test :—On dissolving 0·1 g. of cocaine hydrochloride in 5 c.c. of water and adding 1 drop of potassium permanganate solution (1 : 1000), the pink coloration should not fade within fifteen minutes. As a standard for comparison, 1 drop of potassium permanganate is added to 5 c.c. of water.

It is of importance that the test tubes used for the above reactions are scrupulously clean.

Foreign Alkaloids.—On adding 10 drops of 3 per cent. chromic acid solution to an aqueous solution of cocaine hydrochloride (0·1 : 10), the addition of each drop produces a yellow precipitate which redissolves immediately; on the addition of 2 c.c. of hydrochloric acid (sp. gr. 1·124) the precipitate is reformed.

G. L. Schaefer[2] has proposed the following test, based on the relative greater solubility of cocaine chromate as compared with that of the chromates of the other coca bases, in presence of hydrochloric acid :—0·05 g. of cocaine hydrochloride is dissolved in 20 c.c. of water, 5 c.c. of a 3 per cent. chromic acid solution and 5 c.c. of 10 per cent. hydrochloric acid (at 15°) added; if the cocaine hydrochloride is pure, the solution remains clear, and the more foreign coca bases are present the greater is the turbidity produced. The

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[1] For identifying reactions, cf. *Merck's Reag.-Verz.*, 1908, p. 292.

[2] *Pharm. J.*, 1899, **69** [1503], 336; 1899, **63** [1517], 66; *J. Soc. Chem. Ind.*, 1899, **18**, 522, 790.

value of this reaction has been adversely criticised by P. W. Squire[1] and by E. Merck.[2]

MacLagan's Test.—0.1 g. of cocaine hydrochloride is dissolved in 100 c.c. of water, and 0.2 c.c. of ammonia (sp. gr. 0.96) added; on vigorously scratching the sides of the glass vessel with a glass rod, a flocculent crystalline precipitate is formed within ten minutes without any milky turbidity being produced in the liquid; the latter should remain quite clear.[3]

This test is prescribed as follows by the British Pharmacopœia:— 0.1 g. of cocaine dissolved in 100 c.c. of water and 0.25 c.c. of a solution of ammonia added, affords a clear solution from which a crystalline precipitate should gradually separate on stirring.

The German Pharmacopœia gives the following modification of this test:—If a solution of 0.1 g. of cocaine hydrochloride in 80 c.c. of water is carefully mixed, without shaking, with 2 c.c. of a mixture of 1 part of ammonia (10 per cent.) and 9 parts of water, no turbidity should become apparent within half an hour. On scratching the sides of the glass vessel with a glass rod, the above-mentioned separation of crystals, etc., should then take place.

Organic Matter; Sugar; Foreign Alkaloids.—Cocaine hydrochloride should produce colourless solutions when dissolved in nitric and in sulphuric acids in the proportion of 1 : 10.

Water.—No appreciable loss in weight should take place on drying cocaine hydrochloride at 100°. The British Pharmacopœia prescribes that the salt should not lose more than 1 per cent. of moisture when dried for twenty minutes at 95°.6-100°.

Cocaine hydrochloride may be estimated volumetrically in alcoholic solution, using Poirrier's blue as indicator, as described for quinine hydrochloride (p. 381). 1 c.c. of $N/5$ potassium hydroxide corresponds to 0.06793 g. of cocaine hydrochloride.

Coumarin.

$$C_6H_4 \begin{matrix} O - CO \\ | \\ CH = CH \end{matrix}. \quad \text{Molec. wt. 146.05.}$$
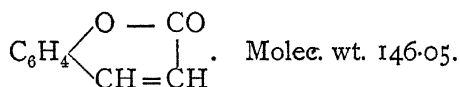
Coumarin forms white, glistening, small, leafy crystals, and possesses a characteristic smell. It is sparingly soluble in cold water (about 1 : 400), more readily in boiling water (about 1 : 45), and very soluble

[1] *Chem. and Drug.*, 1899, **54**, 641.

[2] *Pharm. J.*, 1899, **62** [1511], 523; *J. Soc. Chem. Ind.*, 1899, **18**, 713.

[3] For further details of the MacLagan test, *cf.* Günther, *Pharm. Zentralh.*, 1899, p. 186; E. Merck, *Pharm. Zeit.*, 1899, **44**, 367; *J. Soc. Chem. Ind.*, 1899, **18**, 713; C. Boehringer, *Chem. ana Drug.*, 1899, **55**, 59; Zimmer & Co., *Pharm. Zeit.*, 1899, **66**, 583; *J. Soc. Chem. Ind.*, 1899, **18**, 1055; B. H. Paul and A. J. Cownley, *Pharm. J.*, 1899, **62** [1511], 524.

in alcohol and in ether; melting point 67°; boiling point 291°. On fusing coumarin with potassium hydroxide, salicylic and acetic acids are formed, which may be readily identified.

Tests for Impurities.

Vanillin.—No coloration should be produced on heating 0·2 g. of coumarin with a mixture of 5 c.c. of phenol and 3 c.c. of sulphuric acid at 160°-170° for several minutes; vanillin gives a blood-red or very dark red coloration.[1]

Organic Impurities.—A colourless solution should be formed on dissolving 1 g. of coumarin in 10 c.c. of sulphuric acid.

Inorganic Impurities.—On ignition, 1 g. of coumarin should not leave more than 0·5 mg. of residue.

Acetanilide.—0·2 g. of coumarin is boiled for one minute with 2 c.c. of hydrochloric acid, and then 4 c.c. of phenol solution (1 : 20) together with a filtered solution of calcium hypochlorite added; no violet coloration should be produced. The latter would be formed in presence of acetanilide, in which case the colour of the mixture would be changed to indigo-blue on the further addition of ammonia. The acetanilide may be most simply estimated by determining the nitrogen by Kjeldahl's method, provided that no other substances containing nitrogen are present.[2]

Dextrose.

$C_6H_{12}O_6$.   Molec. wt. 180·10.
$C_6H_{12}O_6 + H_2O$.   Molec. wt. 198·11.

·Anhydrous dextrose consists of small, white, odourless prisms, joined together to form warty masses, or of a white crystalline powder. It has a sweet taste, the degree of sweetness being less than half that of cane sugar. Dextrose containing water of crystallisation forms white, granular, crystalline masses. The anhydrous substance melts at 146°, the hydrated at about 85°. The specific rotatory power of the anhydrous dextrose is $[\alpha]_D = 52·5$; that of the hydrated form $[\alpha]_D = 47·7$. The so-called anhydrous dextrose of commerce generally contains small quantities of water, which lower the melting point. Dextrose is very soluble in water, almost insoluble in cold alcohol, but more so in boiling alcohol.

Dextrose reduces alkaline copper and bismuth solutions, ammoniacal silver solution, and copper acetate solution on warming.[3]

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[1] Cf. *Merck's Reag.-Verz.*, 1908, p. 133.

[2] For the detection, separation, and identification of coumarin and vanillin in commercial extracts, cf. *Z. anal. Chem.*, 1904, 43, 263.

[3] For reactions of dextrose, cf. *Merck's Reag.-Verz.*, 1908, p. 294.

Tests for Impurities.

Inorganic Matter.—On ignition, 5 g. of dextrosé should not leave more than 0·5 mg. of residue.

Sulphuric Acid.—An aqueous solution of dextrose (1 : 10) should give no reaction with barium chloride solution.

Hydrochloric Acid.—No precipitate, but at most only a faint opalescence, should be shown on adding a few drops of nitric acid and silver nitrate solution to an aqueous solution of dextrose (1 : 10).

Cane Sugar.—A colourless solution should be produced on dissolving 1 g. of dextrose in 10 c.c. of sulphuric acid at 15°; only a pale yellow coloration should result on standing for a quarter of an hour.

Dextrin.—1 g. of dextrose should dissolve completely in 20 c.c. of boiling 90 per cent. alcohol without leaving any insoluble residue. An aqueous solution of dextrose (1 : 10) should not turn a reddish colour on the addition of a very dilute iodine solution.

Quantitative Estimation.

The water in dextrose is determined by drying at 100° till constant.

Dextrin in impure dextrose is determined indirectly by estimating the content of dextrose, of water, and of ash, and calculating the dextrin by difference; or, the dextrose is determined before and after inversion, and the dextrin calculated from the difference.

The content of dextrose may be arrived at by various methods :—

1. By measuring the polarisation of the aqueous solution.[1]

2. From the specific gravity of the aqueous solution.[2]

3. By the reducing action on Fehling's solution, either using a volumetric method or by weighing the cuprous oxide.

Details of these methods are described in the sections on "Sugar" (pp. 554 *et seq.*) and "Brewing Materials and Beer" (pp. 824 *et seq.*).

The following volumetric method by E. Riegler[3] is simple and satisfactory.

This method is based on the estimation of the copper in a known volume of Fehling's solution before and after the reduction by means of dextrose, the copper being estimated iodometrically according to the equation :—

$$2CuSO_4 + 4KI = 2K_2SO_4 + Cu_2I_2 + I_2.$$
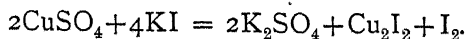
A copper solution is prepared (69·28 g. of crystallised copper sulphate to the litre), as well as a solution of Rochelle salt (346 g. of Rochelle salt and 100 g. of sodium hydroxide to the litre), the former being standardised as follows :—10 c.c. of the copper solution, 10 c.c. of

[1] Landolt, *Ber.*, 1888, 21, 191 ; *Z. anal. Chem.*, 1889, 28, 203.

[2] *Z. anal. Chem.*, 1883, 22, 454.

[3] *Z. anal. Chem.*, 1898, 37, 22 ; *J. Soc. Chem. Ind.*, 1898, 17, 499.

the Rochelle salt solution, 100 c.c. of water, and 2 c.c. of pure concentrated sulphuric acid are well mixed in a 200 c.c. flask, 10 c.c. of a 10 per cent. aqueous solution of potassium iodide added, and the contents of the flask well mixed. In the course of about ten minutes starch solution is added and the free iodine titrated with $N/10$ sodium thiosulphate, until the blue colour disappears and does not return on standing for five minutes; a return of the blue colour after standing for over five minutes is disregarded. Each cubic centimetre of thiosulphate solution corresponds to 0·00635 g. of copper. If the solutions have been correctly prepared, 10 c.c. of the copper solution will require 27·8 c.c. of the thiosulphate solution, and the quantity of copper found will be, therefore, $27·8 \times 0·00635 = 0·1765$ g. If more or less than 27·8 c.c. be required, the volume found must be used as a factor in place of 27·8.

To carry out the estimation, 10 c.c. of the copper solution, 10 c.c. of Rochelle salt solution, and 30 c.c. of water are heated to boiling in a 200 c.c. beaker, and 10 c.c. of a solution of dextrose, not stronger than 1 per cent., are run in. The mixture is kept boiling for some time, after which the precipitate is allowed to settle, the solution filtered (using the pump) through an asbestos filter, and the precipitate washed with about 80 c.c. of water. The filtrate is washed out into a 200 c.c. flask, 2 c.c. of sulphuric acid added, then 10 c.c. of potassium iodide solution, and after standing for ten minutes starch solution is added and the iodine titrated with thiosulphate solution as above.

If V represents the number of cubic centimetres of thiosulphate solution used, then the quantity of copper reduced by the sugar is $= (27·8 - V) \times 0·00635$.

Diethyl Barbituric Acid. (Veronal.)

$$(C_2H_5)_2C \Big\langle \begin{array}{c} CO-NH \\ CO-NH \end{array} \Big\rangle CO. \quad \text{Molec. wt. } 184·12.$$
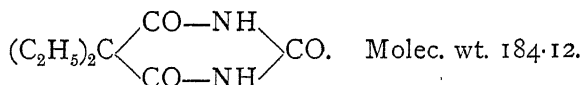
Diethyl barbituric acid or veronal is a white, crystalline powder with a somewhat bitter taste, soluble in about 145 parts of cold or in 12 parts of boiling water. It is readily soluble in ether, acetone, ethyl acetate, hot alcohol, and alkalis, but is only sparingly soluble in chloroform and glacial acetic acid. The aqueous solution reacts faintly acid with litmus paper. Melting point 191°. The addition of a few drops of nitric acid and several drops of Millon's reagent to a solution of 0·05 g. of veronal in 10 c.c. of water produces a white gelatinous precipitate which redissolves on adding a large excess of the precipitant. Ammonia is evolved on boiling 0·1 g. of veronal with 5 c.c. of potassium hydroxide solution.

Tests for Impurities.

Hydrochloric and Sulphuric Acids.—Neither barium nitrate nor silver nitrate solution should produce a precipitate with a solution of 0·1 g. of veronal in 20 c.c. of water.

Organic Impurities.—Veronal should dissolve in sulphuric acid to a colourless solution. It should not become coloured on shaking with nitric acid.

Inorganic Impurities.—0·1 g. of veronal is placed on the lid of a platinum crucible and heated on an asbestos plate. The preparation should sublime, leaving only very little carbon behind. On ignition, no appreciable residue should be left.

Veronal-Sodium.

$$C_2H_5 \diagdown \qquad \diagup CO . NNa \diagdown$$
$$\qquad \diagup C \diagdown \qquad \diagup CO. \quad \text{Molec. wt. } 206\cdot11.$$
$$C_2H_5 \diagup \qquad \diagdown CO . NH \diagup$$
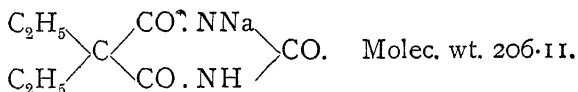
This is a white, crystalline powder with a bitter taste, and is very soluble in water (1 : 5). The aqueous solution reacts alkaline. Mineral acids as well as acetic acid produce a voluminous white precipitate when added to a concentrated aqueous solution (1 : 5).

Veronal-sodium may be titrated with $N/10$ hydrochloric acid, using either methyl orange or Congo red as indicator.[1]

Ethyl Acetate.

$$CH_3 . COOC_2H_5. \quad \text{Molec. wt. } 88\cdot06.$$

Ethyl acetate is a colourless, volatile liquid with a characteristic refreshing smell. It is miscible in all proportions with alcohol, ether, benzene, and chloroform, and with 17 parts of water.

Ethyl acetate, when quite pure and free from water and alcohol, has a sp. gr. of 0·9254 at 0° compared with water at 4° (J. Wade and R. W. Merriman[2]), and boils at 77°. The pure commercial product, which also is used in medicine, has a sp. gr. of 0·900-0·904 and boils at 74°-78°; it contains traces of water and alcohol.

Tests for Impurities.

Inorganic and non-volatile Organic Matter.—No residue should be left on evaporating 50 c.c. of ethyl acetate on the water-bath.

Free Acid (Acetic Acid).—A piece of blue litmus paper placed in ethyl acetate should not be immediately reddened.

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[1] For further details concerning veronal, cf. *Pharm. Zentralh.*, 1908, p. 1041.

[2] *J. Chem. Soc.*, 1912, **101**, 2429.

Amyl Compounds and Ethyl Butyrate.—On pouring ethyl acetate over filter paper and allowing it to evaporate at the ordinary temperature, it should not be possible to detect the smell of foreign esters after the smell of the ethyl acetate ceases to be noticeable.

Amyl Alcohol and Organic Impurities.—On pouring a few cubic centimetres of ethyl acetate carefully on to sulphuric acid, no coloration should be produced at the zone of contact of the two layers of liquid.

Water and Alcohol.—On thoroughly shaking 25 c.c. of ethyl acetate with 25 c.c. of a saturated solution of calcium chloride for one minute, no appreciable increase in the volume of the latter should take place.

Note.—On shaking ethyl acetate with water, the volume of the latter increases from 2-2.5 c.c., owing to the water taking up some ethyl acetate; on the other hand, ethyl acetate also takes up water. The use of a cold, saturated solution of calcium chloride allows of a better estimation of the content of water and of alcohol being made, since the latter are completely taken up by the calcium chloride solution. A turbidity produced on dissolving in benzene will indicate if more than a permissible quantity of water is present. 1 c.c. of ethyl acetate should dissolve to a clear solution in 10 c.c. of benzene. Ethyl acetate quite free from water will also dissolve to a clear solution in official paraffin oil (liquid paraffin).

The content of alcohol is determined in the same manner as described for ethyl butyrate (see p. 349).

Ethyl Alcohol.

$C_2H_5 . OH$.   Molec. wt. 46.05.

Two kinds of ethyl alcohol come under consideration for technical purposes: the so-called "Absolute Alcohol" and "Rectified Spirit"; from the latter, various mixtures with water are prepared, such as the 70 per cent., 60 per cent., 45 per cent., and 20 per cent. spirit of the British Pharmacopœia.

The qualitative examination of these varieties may be made in the same manner, without reference to the differences in the content of alcohol.

Absolute alcohol is a colourless, neutral liquid boiling at 78°.4; the specific gravity, according to the determinations of Mendeleff, is 0.79367 at 15°/4°. A good commercial product should contain not less than 99.11 per cent. by weight of alcohol and have a sp. gr. of not over 0.797. A guarantee of 100 per cent. can never be given, since 100 per cent. alcohol is very hygroscopic.

Rectified spirit should contain at least 94.38 per cent. by weight, and 96.37 per cent. by volume of alcohol and have a sp. gr. not higher than 0.811. The "Rectified Spirit" of the British Pharmacopœia

has a sp. gr. of 0·8340 and contains 85·65 per cent. by weight of ethyl alcohol.

Tests for Impurities.

Fusel Oil.—No turbidity and no smell foreign to alcohol should be produced on mixing 10 c.c. of alcohol with 30 c.c. of water in an Erlenmeyer flask. On rubbing a few drops of the sample between the hands, no unpleasant smell (fusel oil) should be noticeable after the evaporation of the alcohol. On the addition of 25-30 drops of a 1 per cent. alcoholic solution of salicyl aldehyde and 20 c.c. of concentrated sulphuric acid to a mixture of 5 c.c. of alcohol and 5 c.c. of water, and cooling the mixture, a lemon-yellow coloration is produced if the alcohol be free from fusel oil. If only traces of fusel oil are present, the solution will appear yellow by transmitted light and red by reflected light. In no case should the colour be reddish or red.

If a mixture of 10 c.c. of alcohol and 0·2 c.c. of 15 per cent. potassium hydroxide solution be evaporated down to 1 c.c. on the water-bath, there should be no smell of fusel oil on adding excess of dilute sulphuric acid.

Acetone.—On shaking a mixture of 2 c.c. of alcohol, 6 c.c. of baryta water, and 6 drops of mercuric chloride solution (1 : 20) for one minute and filtering, the filtrate should not be darkened by the addition of ammonium sulphide solution.

Aldehyde.—A mixture of 10 c.c. of alcohol, 10 c.c. of water, and 2 c.c. of ammoniacal silver solution (prepared by mixing 10 c.c. of 5 per cent. silver nitrate solution with 5 c.c. of ammonia of sp. gr. 0·96), allowed to stand in the dark at the ordinary temperature for fifteen hours, should become neither coloured nor turbid.

Furfural (Furfuraldehyde).—A mixture of 10 c.c. of alcohol, 5 drops of acetic acid (sp. gr. 1·040-1·042), and 1 drop of aniline, as colourless as possible, should not turn red in the course of one hour.

Molasses Spirit.—On pouring 5 c.c. of alcohol carefully over 5 c.c. of concentrated sulphuric acid, no rose-coloured ring should be produced at the point of contact of the two layers of liquid.

Metals and Tannin.—No coloration should be produced on adding either 1 c.c. of ammonia (sp. gr. 0·96) or 5 c.c. of sulphuretted hydrogen water to 10 c.c. of alcohol.

Inorganic Matter.—No appreciable residue should remain on slowly evaporating 50 c.c. of alcohol.

Methyl Alcohol.—If a negative result has been obtained when testing for acetone, it may be taken for granted that the alcohol contains no crude wood spirit.

For the independent detection of methyl alcohol in ethyl alcohol, a number of methods have been proposed, based on the oxidation of the

methyl alcohol to formaldehyde and the subsequent identification of the latter. A critical summary of the various methods has been given by A. Vorisek,[1] who recommends oxidation with potassium bichromate and sulphuric acid and testing the distillate obtained for formaldehyde by the addition of ferric chloride and albumin solutions in presence of concentrated sulphuric acid, when a sharply defined violet-coloured zone is formed at the junction of the liquids.

Quantitative Estimation.

The content of alcohol is practically always determined by means of the specific gravity, specially prepared Tables being employed of which those of the Excise Authorities constitute the legal standard in this country. A full description of this estimation is described under the heading "Alcoholometry," in the section on "Alcohol, Potable Spirits, and Liqueurs," this Vol., p. 709.

Should it be desired to carry out an estimation of ethyl alcohol by a chemical method, that given by O. Blank and H. Finkenbeiner[2] for methyl alcohol is to be recommended, since it is also quite suitable for the estimation of ethyl alcohol. An excess of $N/10$ potassium bichromate solution and sulphuric acid are added to the very dilute aqueous solution of the alcohol, and after standing at the ordinary temperature for some hours, potassium iodide is added and the mixture titrated back with $N/10$ sodium thiosulphate solution. The oxidation takes place according to the equation :—

$$CH_3 . CH_2OH + O_2 = CH_3 . COOH + H_2O.$$
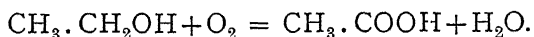
A reliable method for the quantitative estimation of methyl alcohol in ethyl alcohol, based on the oxidation of the former to carbon dioxide, has been worked out by T. E. Thorpe and J. Holmes.[3] (See p. 717.)

Ethyl Bromide.

C_2H_5Br.   Molec. wt. 108·96.

Ethyl bromide is a clear, colourless, strongly refractive, ethereal smelling liquid with a sp. gr. of 1·453-1·457, and boiling at 38°-40°. Perfectly pure ethyl bromide has a sp. gr. of 1·4735 and boils at 38°-39°. Since the pure product readily turns yellow through decomposition, about 1 per cent. of alcohol is added to render the commercial product less liable to decomposition.

[1] *J. Soc. Chem. Ind.*, 1909, **28**, 823. *Cf.* also C. Denigès, *Bull. Soc. Chim.*, 1910, **7**, 951 ; *J. Soc. Chem. Ind.*, 1910, **29**, 1325, and *Merck's Reag.-Verz.*, 1908, p. 297.

[2] *Ber.*, 1906, **39**, 1326 ; *J. Soc. Chem. Ind.*, 1906, **25**, 500.

[3] For estimating ether and benzene in alcohol, *cf.* H. Wolff, *Chem. Zeit.*, 1910, **34**, 1193 ; *J. Soc. Chem. Ind.*, 1910, **29**, 1403, and for estimating carbon bisulphide in alcohol, W. Schmitz-Dumont, *Chem. Zeit.*, 1897, **21**, 487 and 510 ; *J. Soc. Chem. Ind.*, 1897, **16**, 829.

Tests for Impurities.

Inorganic and non-volatile Organic Matter.—Not more than 1 mg. of residue should remain on evaporating 20 c.c. of ethyl bromide on the water-bath.

Phosphorus Compounds.—No unpleasant garlic-like odour should be recognisable on evaporating 5 c.c. of ethyl bromide in a small porcelain dish.[1]

Hydrobromic Acid.—Ethyl bromide should react neutral. On shaking 10 c.c. with 10 c.c. of water for a few seconds, pouring off 5 c.c. of the aqueous layer and adding 2 drops of $N/10$ silver nitrate solution, no turbidity should be produced within five minutes. The ethyl bromide should not be shaken up directly with silver nitrate solution, since silver bromide is always thus formed.

Amyl Compounds, Ethylene dibromide, Organic Sulphur Compounds.—10 c.c. of ethyl bromide are well shaken during one hour with 10 c.c. of sulphuric acid in a stoppered glass cylinder previously rinsed out with sulphuric acid. No yellow coloration of the sulphuric acid should be produced.

Ethyl Ether.—A possible content of ether is indicated by a too low specific gravity. It is stated that commercial ethyl bromide may contain up to 15 per cent. of ether.[2]

Ethyl Butyrate.

$$C_3H_7 . COOC_2H_5. \quad \text{Molec. wt. } 116 \cdot 10.$$
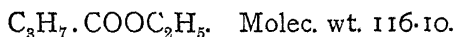
Ethyl butyrate is a colourless liquid, sparingly soluble in water but readily so in alcohol, ether, benzene, chloroform, and petroleum spirit. In the diluted state it possesses a pleasant smell and tastes of pine apple. Its sp. gr. is 0·884, and it boils at 118°-120°.

Tests for Impurities.

Inorganic and non-volatile Organic Matter.—10 c.c. of ethyl butyrate should not leave more than 0·5 mg. of residue on evaporation.

Hydrochloric and Sulphuric Acids.—On shaking 20 c.c. of ethyl butyrate with 10 c.c. of water, the separated water should show no reaction with either silver nitrate or barium chloride solutions. The test cannot be made with litmus paper, since the water always reacts acid owing to liberated butyric acid.

Water.—Ethyl butyrate should dissolve without turbidity in ten times its volume of benzene. Chemically pure ethyl butyrate, absolutely free from water and alcohol, mixes also with petroleum spirit (boiling

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[1] Cf. *Chem. Zeit. Rep.*, 1908, **32**, 638. [2] *Pharm. Zentralh.*, **35**, 674.

point 50°-75°) and official paraffin oil (liquid paraffin) to form quite clear solutions.

Alcohol.—On shaking 20 c.c. of ethyl butyrate with 20 c.c. of a saturated solution of calcium chloride, and allowing the two liquids to separate completely, no change in volume of the calcium chloride solution should take place.

Quantitative Estimation.

Ethyl butyrate comes into commerce in alcoholic solution, the product being known as "pine-apple oil." The content of the ester in such products may be sufficiently accurately estimated by shaking with a proportionately large volume of saturated calcium chloride solution.

The accurate estimation of the alcohol and of the ester, in either concentrated or dilute commercial varieties, is carried out as follows :— 25 g. of the ester are heated with a solution of 22 g. of potassium hydroxide in 40 c.c. of water in a 200-250 c.c. Jena glass flask fitted with an upright condenser, until the saponification is complete. In the case of products containing a high percentage of ester, complete saponification is indicated by the original two layers of ester and of potassium hydroxide disappearing to form one homogeneous straw-coloured solution. The mixture is then further boiled for about half an hour. In the case of products of low ester content (*i.e.*, mixtures containing a little ester and much alcohol), after the disappearance of the two layers of liquid, the mixture is further boiled vigorously for one hour. The saponification should be carried out over the free flame, or over a wire gauze. The contents of the flask are then allowed to cool, about 60 c.c. of water washed down the upright condenser into the flask, and 100 g. of the mixture then distilled off, using an ordinary condenser and a condensation bulb between the flask and condenser, and taking care that no alkali spirts over, and that no alcohol is lost by evaporation. From the specific gravity of the distillate its alcohol content can be calculated, and from this value the alcohol content in the ester in percentage by weight. Having thus determined the free alcohol together with the alcohol combined with the butyric acid, the content of combined alcohol, from which the content of pure ester may be calculated, is determined by saponifying a weighed quantity of the ester with an excess of $N/2$ potassium hydroxide, and titrating back with $N/2$ hydrochloric acid, using phenolphthalein as indicator. 1 c.c. of $N/2$ potassium hydroxide corresponds to 0·05805 g. of butyric ester, or to 0·04605 g. of combined alcohol.

The difference between the total alcohol and the combined alcohol gives the quantity of free alcohol. All the necessary data may be, therefore, obtained by making the above two estimations, from which the content of pure ester, of alcohol, and of water are calculated.

Ethyl Ether.

$$C_2H_5 . O . C_2H_5.$$ Molec. wt. 74.08.

Ether is a colourless, mobile, and readily inflammable liquid, possessing a characteristic smell. It boils at 34°-36°, and has a sp. gr. of 0.720. Ordinary commercial ether has a sp. gr. of 0.725, owing to its containing small quantities of water or of alcohol. Ether used for the quantitative estimation of fat, in the analysis of alkaloids, and for anæsthetic purposes, should have a sp. gr. of not more than 0.720-0.722. The ether of the British Pharmacopœia has a sp. gr. of 0.735, and contains not less than 92 per cent. by volume of pure ether.

Tests for Impurities.

Residue.—On allowing 20 c.c. of ether to evaporate spontaneously in a glass dish, covered with an inverted funnel, the residue remaining on the sides of the dish should have no smell, should not redden or bleach blue litmus paper, and on warming on the water-bath should evaporate completely, leaving no residue.

Water.—On shaking 20 c.c. of ether with 1 g. of dehydrated copper sulphate, the latter should not acquire either a green or blue colour.

A method for the quantitative estimation of water in "wet" ether based on the insolubility of cadmium iodide in anhydrous ether, has been worked out by D. Tyrer.[1]

Hydrogen Peroxide, Ozone, Ethyl Peroxide.—On shaking 10 c.c. of ether with 1 c.c. of potassium iodide solution (1 : 10) in a full, closed, glass-stoppered vessel, in the dark, neither the potassium iodide solution nor the ether should become coloured at the end of one hour.

A very sensitive reaction for peroxides is the following :—0.1 g. of pure, powdered vanadic acid is heated for a quarter of an hour on the water-bath with 2 c.c. of concentrated sulphuric acid, and then 50 c.c. of water added. This reagent has a yellow colour. On shaking 20-30 c.c. of ether with 2 c.c. of this reagent, the smallest traces of peroxide present will immediately turn the colour of the latter to brown or reddish-brown.

Aldehyde and Vinyl Alcohol.—On shaking 20 c.c. of ether for one minute in a glass-stoppered cylinder with 5 c.c. of Nessler's reagent, no reddish-brown precipitate, soon turning to black, should be produced.[2]

Acetone.—A mixture of 6 c.c. of baryta water and 6 drops of 5 per cent. mercuric chloride solution are shaken for one minute with 20 c.c. of ether, and the aqueous solution separated and filtered. The latter should show no dark coloration during ten minutes after the addition of ammonium sulphide.

[1] *J. Chem. Soc. Proc.*, 1911, **27**, 142 ; *J. Soc. Chem. Ind.*, 1911, **30**, 767.
[2] *Cf.* Wobbe, *Apoth. Zeit.*, 1903, p. 466.

Sulphur Compounds.—On shaking 20 c.c. of ether with a drop of mercury in a glass bottle for two minutes, the surface of the mercury should show no change, and no black substance should be separated.

Alcohol.—A test for alcohol is not necessary should the ether. possess the correct specific gravity; a Table giving the specific gravities of mixtures of alcohol and ether has been prepared by E. R. Squibb.[1] According to Lieben, the presence of alcohol may be detected by the iodoform reaction. The ether is shaken up with water, and the aqueous solution warmed, after the addition of sodium hydroxide and iodine solutions; the formation of iodoform indicates the presence of alcohol.

Formaldehyde.

$H . CH\odot$.   Molec. wt. 30·02.

Formaldehyde is a colourless liquid with an irritating smell, and is miscible in all proportions with water and alcohol. The specific gravity of the commercial product varies from 1·08-1·095 according to the content of formaldehyde and of methyl alcohol, and the content of formaldehyde varies from 30-40 per cent. The purest commercial product is that used for medicinal purposes. The German Pharma-copœia gives the sp. gr. of 1·079-1·081 with about 35 per cent. of formaldehyde. The specific gravity alone gives no reliable indication as to the content of formaldehyde, since the commercial product always contains some methyl alcohol which lowers the specific gravity. The 40 per cent. formaldehyde contains up to 20 per cent. of methyl alcohol. In preparations containing less methyl alcohol, there is always the possibility of paraformaldehyde separating out at somewhat low temperatures.[2]

The methods for the estimation of methyl alcohol in formaldehyde are fully described in the section on "Organic Dyes," Vol. II., Part II., pp. 911 *et seq.*

Formaldehyde reduces ammoniacal silver solution and Fehling's solution and gives a deep red coloration with Schiff's reagent; an ammoniacal formaldehyde solution gives a white precipitate with bromine water (hexamethylenetetramine bromide). On evaporating formaldehyde on the water-bath a white amorphous mass (trioxy-methylene) is left, which is insoluble in water, and which is completely volatile on ignition. On making formaldehyde strongly alkaline with ammonia, and heating the mixture on the water-bath, a white crystal-line residue (hexamethylenetetramine) remains, which is readily soluble in water. Other reactions that can be used for the quantitative deter-

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[1] *Pharm. J.*, 1884, p. 74; *J. Soc. Chem. Ind.*, 1884, **3**, 531. Cf. also *Z. anal. Chem.*, 1889, **26**, 97.

[2] Cf. *Merck's Jahresber.*, 1903, p. 79.

mination of formaldehyde are described in the section on "Organic Dyes," Vol. II., Part II., pp. 898 *et seq.*

Tests for Impurities.

Free Acid.—10 c.c. of formaldehyde should not react acid after the addition of 10 drops of *N*/1 potassium hydroxide. Formaldehyde sometimes contains up to 0·2 per cent. of formic acid.

Hydrochloric Acid.—Formaldehyde should, at most, only give a slight opalescence on the addition of silver nitrate solution, and when diluted with four times its volume of water should give no reaction with this reagent.

Sulphuric Acid.—Formaldehyde should show no reaction with barium chloride solution.

Heavy Metals.—On the addition of sulphuretted hydrogen water, formaldehyde should not be discoloured. Commercial products sometimes contain up to 0·01 per cent. of cupric oxide, in which case the above test will not be negative.

Inorganic Salts.—Not more than 1 mg. of residue should remain on evaporating 10 c.c. of formaldehyde and igniting with free access of air. The purest formaldehyde often contains minute traces of iron.

Quantitative Estimation.

The methods for the quantitative estimation of formaldehyde are described in the section on "Organic Dyes," Vol. II., Part II., pp. 901 *et seq.*

Formic Acid.

H . COOH.   Molec. wt. 46·02.

Formic acid is a colourless liquid with an irritating smell. It has a sp. gr. of 1·22 at 20°, boils at 100°·6, and melts at 8°·6. It is miscible in all proportions with water and alcohol. Sulphuric acid decomposes it into carbon monoxide and water. On warming an aqueous solution of formic acid (1 : 10) with silver nitrate, metallic silver separates out; warmed with mercuric chloride, mercurous chloride is precipitated; and on warming with yellow mercuric oxide, a colourless solution is first formed from which, on further heating, carbon dioxide is evolved with separation of metallic mercury.

Tests for Impurities.

Inorganic Matter.—Not more than 0·5 mg. of residue should be left on evaporating 5 g. of formic acid.

Lead, Copper, Iron.—Sulphuretted hydrogen water should produce no change in a solution of formic acid (1 : 20) rendered alkaline by ammonia.

Hydrochloric and Oxalic Acids.—Neither silver nitrate solution at the ordinary temperature nor calcium chloride solution, the latter being added to a solution made alkaline with ammonia, should produce any change in an aqueous solution of formic acid (1 : 20).

Acetic Acid.—If 1 c.c. of formic acid is warmed on the water-bath with 20 c.c. of water and 6 g. of yellow mercuric oxide, and frequently shaken until no further evolution of gas takes place on filtering, the filtrate should not react acid.

Acrolein, Allyl Alcohol, Empyreumatic Matter.—No irritating or burning smell should be given off on saturating formic acid with excess of sodium hydroxide solution.

Since formic acid comes into commerce in various degrees of dilution, the content of formic acid should first be determined by titration with $N/1$ sodium hydroxide solution, and the foregoing tests then carried out with suitable quantities proportional to the degree of dilution of the acid.

Quantitative Estimation.

Formic acid is estimated in aqueous solution by titration with $N/1$ sodium hydroxide, using phenolphthalein as indicator. 1 c.c. of $N/1$ sodium hydroxide corresponds to 0·046016 g. of formic acid. Since this simple titration gives no guarantee that only the formic acid is estimated, it is better to use the method worked out by H. Franzen and G. Greve, as described in the section on " Organic Dyes," Vol. II., Part II., p. 917. Other quantitative methods are described in the same section.[1]

Gallic Acid.

$$C_6H_2(OH)_3 . COOH + H_2O. \quad \text{Molec. wt. } 188·06.$$
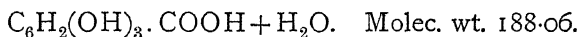
Pure gallic acid comes into commerce as colourless or pale yellow coloured needles or prisms, which possess an acid, astringent taste, and which melt at 220°, undergoing slow decomposition.

Gallic acid dissolves in 85 parts of water at 15° and in 3 parts of boiling water, in 6 parts of alcohol and in 10 parts of glycerol. It is only sparingly soluble in pure ether, but the solubility increases with an increase in the proportion of alcohol contained in the ether used.

A bluish - black precipitate is produced on adding ferric chloride to a solution of gallic acid. On standing in the air, an aqueous solution of the acid, to which excess of alkali is added, turns reddish-brown to black. Potassium cyanide colours the aqueous solution red.[2]

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[1] *Cf.* also A. F. Joseph, *J. Soc. Chem. Ind.*, 1911, **29**, 1189.

[2] For reactions distinguishing gallic from tannic acid, cf. *Z. anal. Chem.*, 1889, **28**, 103, 351 ; 1892, **31**, 88 ; 1896, **35**, 590 ; *Pharm. Zentralh.*, 1899, p. 302 ; and *Merck's Reag.-Verz.*, 1908, p. 294.

Tests for Impurities.

Inorganic Matter.—No residue should be left on igniting 1 g. of gallic acid.

Sulphuric Acid.—Barium chloride solution should give no precipitate when added to an aqueous solution of gallic acid (1 : 50), acidified with 1 c.c. of hydrochloric acid, and allowed to stand for one hour at a temperature of 50°.

Water.—On drying at 100° till constant, gallic acid should not lose more than 10 per cent. in weight.

Solubility in Water.—1 g. of gallic acid should dissolve completely in 20 c.c. of water, on warming; the aqueous solution should be colourless, or at most only have a faint yellowish coloration.

Quantitative Estimation.

The following method given by W. P. Dreaper[1] may be used:—5 g. of the gallic acid to be examined are dissolved in 1 litre of water. To 100 c.c. of this solution 1 g. of barium carbonate made up into a thin paste with water is added (to combine with the free sulphuric acid produced in the reaction); the mixture is then heated to 90° and $N/4$ copper sulphate solution run in until copper can be detected in the solution by means of potassium ferrocyanide. This end-point is shown by a brown coloration being produced when a drop of the liquid is put on to filter paper and a drop of potassium ferrocyanide solution allowed to fall on to it. Having thus found how much copper sulphate solution is required for the gallic and tannic acids together in 100 c.c. of the above solution (*i.e.*, for 0·5 g. of substance), the tannic acid is precipitated out of 200 c.c. of the same solution by adding 28·6 c.c. of a 2 per cent. solution of gelatin, saturating the mixture with common salt, adding 5 g. of barium sulphate and 10 c.c. of dilute sulphuric acid (1 : 20), and making up to 400 c.c. The mixture is well shaken, and the tannic acid filtered off. The content of gallic acid in 200 c.c. of the filtrate is determined by titrating with copper sulphate solution. The difference between the two titrations gives the amount of tannic acid contained in the gallic acid taken.

The copper sulphate solution is best standardised against pure gallic acid and pure tannin. Gallic acid of sufficient purity for this purpose is obtainable, and tannic acid of like purity is prepared by shaking up pure tannin with ether until no reaction is obtained with potassium cyanide, and then drying till constant. By this method, gallic and tannic acids may be accurately estimated, either individually or together, but in determining both together the result for tannic acid comes out

[1] *J. Soc. Chem. Ind.*, 1893, 12, 412.

somewhat high, since the precipitation with gelatin solution carries down some gallic acid with the tannic acid.

Gelatin.

The best commercial gelatin forms colourless, or almost colourless, thin, transparent flakes of glassy lustre, which should be tasteless and odourless.

Gelatin swells up in water, dissolving readily in hot water. The hot solution should be clear or only slightly opalescent. On cooling a solution of 1 g. of gelatin in 100 c.c. of water, it should solidify to a jelly. Gelatin is insoluble in alcohol and in ether. Tannic acid solution produces a flocculent precipitate when added to a dilute aqueous solution of gelatin.[1]

Tests for Impurities

Inorganic Matter.—Not more than 0.2 g. of residue should remain on igniting 10 g. of gelatin. The cold, ignited residue is tested for copper [2] by dissolving in 3 c.c. of hydrochloric acid and adding excess of ammonia, when no blue coloration should be produced.

Free Acids.—According to J. Messner no commercial gelatins are free from acid.[3] In the best commercial varieties he found up to 1 per cent. of free acid (calculated as sulphuric acid). Taking this figure as an allowable maximum, products may be tested as follows:—Red litmus paper should be turned blue after adding 0.2 c.c. of $N/1$ potassium hydroxide to a warm solution of 1 g. of gelatin in 100 c.c. of water.

Sulphurous Acid.—Good gelatin generally contains from 0.01-0.02 per cent. of sulphur dioxide.[4] The quantitative estimation is somewhat lengthy, and the following test (given by the German Pharmacopœia) suffices:—5 g. of gelatin are allowed to soak in 30 c.c. of water in a wide-mouthed, 150 c.c. flask and then dissolved by gently warming on the water-bath. 5 g. of phosphoric acid (25 per cent.) are then added, the flask loosely closed by a cork, on the under side of which is fastened a moistened piece of potassium iodide and starch paper, and the contents heated on the water-bath, and frequently shaken round with care. No temporary or permanent blue coloration of the paper should take place within a quarter of an hour.

A method for the quantitative estimation of free and combined sulphurous acid in gelatin has been recently described by R. W. Sindall and W. Bacon.[5]

Water.—The water in gelatin is determined by drying at 105°. A

[1] For identifying reactions for gelatin, *cf.* Liesegang, *Pharm. Zeit.*, 1910, **55**, 283.
[2] *Cf.* W. B. Hart, *J. Soc. Chem. Ind.*, 1909, **28**, 739.   [3] *Merck's Jahresber.*, 1900, p. 31.
[4] *Cf.* W. Lange, *Arb. Kais. gesundh. Amt*, 1909, **32**, 144 ; *J. Soc. Chem. Ind.*, 1909, **28**, 995.
[5] *Analyst*, 1914, **39**, 20.

good sample should not contain more than 20 per cent. of water; the proportion in commercial gelatins usually varies from 11 to 14 per cent.[1]

Guaiacol.

$$C_6H_4\!\!\begin{array}{c} \diagup OH(1) \\ \diagdown OCH_3(2) \end{array} \qquad \text{Molec. wt. } 124{\cdot}06.$$
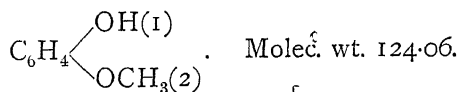
Guaiacol is prepared either as a clear, colourless, refractive, oily liquid boiling at 205°, or in the form of colourless crystals which melt at 28°. It dissolves in about 60 parts of water, and is readily soluble in alcohol and in ether. The addition of one drop of a dilute solution of ferric chloride to the aqueous solution produces a blue coloration which immediately changes to reddish-brown, and when added to an alcoholic solution, a coloration changing from green through blue to greenish-brown is produced.[2]

Tests for Impurities.

A mixture of 1 vol. of guaiacol with 2 vols. of sodium hydroxide solution should be clear and should remain clear and colourless on diluting with 10 vols. of water. A mixture of guaiacol with 2 vols. of potassium hydroxide solution should solidify to a white crystalline mass in a short time. Guaiacol should dissolve to a colourless solution in cold, concentrated sulphuric acid.

Guaiacol Carbonate.

$$CO(O . C_6H_4 . OCH_3)_2. \qquad \text{Molec. wt. } 274{\cdot}112.$$
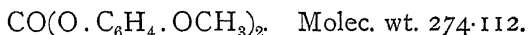
This is the most important pharmaceutical preparation obtained from guaiacol. It is a white, almost odourless, crystalline powder. It dissolves readily in chloroform and in hot alcohol, sparingly in cold alcohol and in ether, and is insoluble in water. It melts between 86° and 88°. Guaiacol carbonate contains approximately 90 per cent. of guaiacol. The latter is separated by saponifying 0·5 g. of guaiacol carbonate with a mixture of 10 c.c. of alcohol and potassium hydroxide solution. After evaporating off the alcohol, the residue is taken up with water, acidified with dilute sulphuric acid, and the guaiacol extracted with ether. On evaporating off the ether an oily residue smelling of guaiacol is left, and which, when dissolved in alcohol, gives the characteristic green coloration with ferric chloride.

If about 0·2 g. of guaiacol carbonate is boiled for from two to three minutes with 10 c.c. of quite clear alcoholic potash (1 g. potassium hydroxide in 20 c.c. of absolute alcohol), a white crystalline precipitate

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[1] Sindall and Bacon, *loc. cit.*
[2] For identifying reactions, cf. *Merck's Reag.-Verz.*, 1908, p. 295.

separates out, which, after washing with alcohol, evolves carbon dioxide when treated with hydrochloric acid.

Tests for Impurities.

Free Guaiacol.—A solution of 0.5 g. of guaiacol carbonate in 10 c.c. of hot alcohol should not change litmus paper and should give no blue or green coloration with ferric chloride.

Hydrochloric Acid.—On shaking 1 g. of guaiacol carbonate with 10 c.c. of water and filtering, the filtrate should give no reaction on acidifying with nitric acid and adding silver nitrate solution.

Organic Impurities.—0.1 g. of guaiacol carbonate should dissolve to a colourless solution in 1 c.c. of sulphuric acid.

Inorganic Impurities.—Not more than 0.5 mg. of residue should be left on igniting 0.5 g. of guaiacol carbonate.

Hexamethylenetetramine.

$(CH_2)_6N_4$. Molec. wt. 140.14.

Hexamethylenetetramine is a colourless, crystalline powder which volatilises on heating without melting. It dissolves in 1.5 parts of water and in 10 parts of alcohol (of about 85 per cent. by weight). The solutions react alkaline with litmus paper. On heating the aqueous solution (1 : 20) with dilute sulphuric acid, formaldehyde, recognisable by its smell, is given off. On further warming, after the addition of excess of sodium hydroxide solution, ammonia is evolved. Silver nitrate solution produces a white precipitate with aqueous solutions of hexamethylenetetramine (1 : 20), which is soluble in excess of the latter. A carmine-red coloration is produced on carefully heating a mixture of 0.1 g. of hexamethylenetetramine with 0.1 g. of salicylic acid and 5 c.c. of concentrated sulphuric acid.

Tests for Impurities.

Heavy Metals and Sulphuric Acid.—No precipitate should be produced on adding either sulphuretted hydrogen water or barium nitrate solution to an aqueous solution (1 : 20).

Hydrochloric Acid.—On adding 5 c.c. of nitric acid and silver nitrate solution to an aqueous solution (1 : 100), at most, only a faint opalescent turbidity should be produced.

Ammonium Salts. Paraformaldehyde.—On heating an aqueous solution (1 : 20) to boiling with Nessler's reagent, neither a coloration nor a turbidity should be produced.

Inorganic Impurities.—Not more than 0.5 mg. of residue should remain on volatilising 1 g. of hexamethylenetetramine.

Quantitative Estimation.

1 g. of the preparation is evaporated to dryness on the water-bath with 40 c.c. of $N/1$ sulphuric acid; formaldehyde is formed whilst the acid combines with the nitrogen to form ammonium sulphate. The residue is taken up with water and further evaporated down until the formaldehyde is completely driven off. It is then dissolved in 100 c.c. of water, and the excess of sulphuric acid titrated back with $N/1$ alkali, using litmus as indicator. The difference between the number of cubic centimetres of alkali used and the number of cubic centimetres of acid taken in the first instance gives the number of cubic centimetres of acid used up in the formation of ammonium sulphate in accordance with the equation :—

$$(CH_2)_6N_4 + 6H_2O + 2H_2SO_4 = 6CH_2O + 2(NH_4)_2SO_4.$$
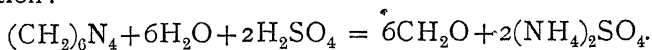
1 g. of hexamethylenetetramine corresponds, therefore, to 28.74 c.c. of $N/1$ sulphuric acid.[1]

Hydroquinone (Quinol).

$$C_6H_4 \begin{cases} OH(1) \\ OH(4) \end{cases}. \quad \text{Molec. wt. 110·05.}$$
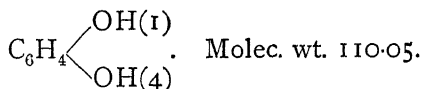
Hydroquinone forms colourless and odourless six-sided prisms which melt at 169°, and at a higher temperature sublime undecomposed. The sublimed hydroquinone forms monoclinic leafy crystals. It dissolves in 17 parts of water at 15°, more readily in hot water, in alcohol, and in ether. It is but sparingly soluble in cold benzene.

An aqueous solution reduces silver nitrate solution even at ordinary temperatures, and Fehling's solution only on warming. A small quantity of ferric chloride produces a temporary blue coloration which disappears on adding more ferric chloride, when small, green, shiny, crystalline leaves (quinhydrone) separate out. In contradistinction to catechol and resorcinol, an aqueous solution of hydroquinone is not precipitated by either lead acetate or by the basic acetate.

Tests for Impurities.

Inorganic Matter.—Not more than 0.5 mg. of residue should remain on heating 1 g. of hydroquinone.

Quinone.—The crystals of hydroquinone should be quite colourless.

Phenol.—Ferric chloride should not produce a permanent violet coloration in an aqueous solution, and the aqueous solution should give no smell of phenol on boiling.

Sulphuric Acid.—Barium chloride solution should produce no precipitate with a cold, saturated, aqueous solution of hydroquinone.

[1] Base, *Pharm. Zeit.*, 1907, **52**, 851.

Iodoform.

CHI$_3$.   Molec. wt. 393.77.

Iodoform forms small hexagonal plates or leafy crystals of a lemon-yellow colour, with a smell somewhat resembling that of saffron.   It melts at about 120°, and decomposes with separation of iodine at a higher temperature.   It is soluble in 10 parts of ether, in 25 parts of absolute alcohol, in about 70 parts of 90 per cent. alcohol, and in 75 parts of glacial acetic acid; it dissolves also in benzene, chloroform, petroleum spirit, and in carbon bisulphide.   It is practically insoluble in water.[1]

Tests for Impurities.

Inorganic Matter.—Not more than 0.5 mg. of residue should be left on igniting 1 g. of iodoform.

Alkali Iodides and Chlorides.—On shaking up 1 g. of iodoform with 10 c.c. of water and filtering, the filtrate should give only an immediate opalescence with silver nitrate solution.

Alkali Carbonates and Sulphates.—Barium chloride solution should produce no precipitate when added to an aqueous filtrate prepared as above.

Water.—Iodoform should dissolve to a clear solution in ten times the quantity of petroleum spirit.   It should, at most, not lose more than 1 per cent. in weight when dried over sulphuric acid for twenty-four hours.

Quantitative Estimation.

About 1 g. of powdered iodoform is heated in a glass flask in a boiling water-bath, and frequently shaken during one hour with 100 c.c. of $N/$10 silver nitrate solution.   Any yellow precipitate adhering to the sides of the flask is then washed down into the solution with as little water as possible, and the whole kept gently boiling over a wire gauze, using a small Bunsen burner, for half an hour.   (This operation may also be carried out with alcoholic solutions of iodoform and silver nitrate.)   On cooling, the solution is filtered into a 250 c.c. measuring-flask, and the precipitate and filter paper afterwards washed with water until the flask is full up to the mark.   The excess of silver nitrate is determined in 50 c.c. of the filtrate by titrating either with $N/$10 sodium chloride solution, or with $N/$10 ammonium thiocyanate solution.   The number of cubic centimetres of sodium chloride solution or of ammonium thiocyanate solution used, multiplied by 5 and subtracted from 100, gives the number of cubic centimetres of silver nitrate solution decom-

[1] For identifying reactions, cf. *Merck's Reag.-Verz.*, 1908, p. 296.

posed by the quantity of iodoform taken. This figure, multiplied by 0.01312, gives the amount of iodoform in the original weighing taken, and the percentage content is thus readily calculated. A good sample should show a percentage of at least 99.5 of iodoform when analysed by this method.

The method may be simplified by decomposing the iodoform with silver nitrate directly in a 250 c.c. measuring flask, and after cooling making up with water to the mark. When the precipitate has settled, 50 c.c. of the clear solution are withdrawn and titrated as above.

The following method of estimation is also to be recommended:— 1 g. of iodoform is dissolved in 100 c.c. of a mixture of 1 part of ether and 3 parts of alcohol, 10 c.c. of this solution transferred to a beaker, a few drops of fuming nitric acid added, followed immediately by 10 c.c. of $N/10$ silver nitrate solution, and the mixture then carefully heated on the water-bath until the smell of ether and of nitrous acid has disappeared. When cold, 100 c.c. of water and about 1 c.c. of iron alum solution are added, and the excess of silver nitrate titrated with $N/10$ ammonium thiocyanate solution. Not more than 2.5 c.c. of the latter should be required.[1] In carrying out this method of estimation care must be taken to add the silver nitrate solution before the nitrous acid has converted the iodine into iodic acid, which would render the analysis inaccurate.[2]

Lactic Acid.

$CH_3 . CHOH . COOH.$ Molec. wt. 90.05.

Fermentation lactic acid is a clear, colourless or slightly yellow, odourless, syrupy liquid, miscible in all proportions with water, alcohol, and ether. It is insoluble in benzene, chloroform, and carbon bisulphide. The official lactic acid of the British Pharmacopœia has a sp. gr. of 1.21 and contains 75 per cent. of pure lactic acid. Chemically pure lactic acid is an extremely hygroscopic crystalline mass, which melts at 18° and boils at 119°-120° under 12 mm. pressure. The 90 per cent. commercial product is the most important technically.

The characteristic formation of crystalline zinc and calcium salts is too long and tedious a test for general purposes. The following test is therefore applied:—3 c.c. of the acid are warmed with 10 c.c. of potassium permanganate solution (1 : 1000), when the characteristic smell of aldehyde is given off.[3]

¹ Utz, *Apoth. Zeit.*, 1906, p. 930.   ² *Z. angew. Chem.*, 1909, **22**, 1059, 1090.
³ Cf. *Merck's Reag.-Verz.*, 1908, p. 297.

Tests for Impurities.

Inorganic Matter.—On strongly heating, lactic acid chars and finally burns away, leaving a small residue which in no case should exceed 0·1 per cent.

Copper, Lead, Zinc, Iron.—Sulphuretted hydrogen water should give no reaction with a 10 per cent. aqueous solution of lactic acid.

Calcium.—An aqueous solution (1 : 10) should give no precipitate with excess of ammonia and ammonium oxalate solution.

Sulphuric Acid and Chlorine Compounds.—Neither barium chloride solution nor silver nitrate solution should produce a precipitate with a 1 : 10 solution of the acid.

Butyric and Acetic Acids.—No smell of fatty acids should be evolved on gently warming lactic acid.

Tartaric and Oxalic Acids.—No turbidity should be produced on mixing 5 c.c. of lactic acid with 100 c.c. of lime water.

Citric Acid.—The mixture with lime water should also not become turbid on warming.

Sugar.—On carefully pouring 5 c.c. of lactic acid over 5 c.c. of sulphuric acid in a test tube, the sulphuric acid should not assume a brown coloration within half an hour. The temperature of the reaction should not be allowed to rise above 15°, otherwise lactic acid, free from sugar, will react and produce a darkening of the sulphuric acid. Sugar may also be tested for by means of Fehling's solution, but unless care be taken, the separation of a very small quantity of cuprous oxide may be overlooked.

Glycerol.—5 g. of lactic acid are warmed with an excess of zinc carbonate, and the mixture dried at 100°. On extracting the residue with absolute alcohol and evaporating off the alcohol on the water-bath, no sweet-tasting residue should remain.

Mannite, Grape Sugar, Cane Sugar, Glycerol.—On dropping 1 c.c. of lactic acid into 2 c.c. of ether, no temporary or permanent turbidity should be produced.[1]

Sarco-Lactic Acid.—A 10 per cent. aqueous solution of lactic acid should give no turbidity on the addition of copper sulphate solution.

Malic and Glycollic Acids.—No turbidity should be produced on adding basic lead acetate to a 10 per cent. solution of lactic acid. (The absence of sulphuric acid being taken for granted.)

Quantitative Estimation.

For the quantitative estimation, 10 g. of lactic acid are dissolved in 1000 c.c. of water. 100 c.c. of this solution are warmed in a flask, in a boiling water-bath, for ten minutes with 15 c.c. of $N/1$ potassium

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[1] Cf. *Pharm. Zentralh.,* 1892, p. 676.

hydroxide, and then titrated with $N/1$ hydrochloric acid, using phenol-phthalein as indicator. 1 c.c. of $N/1$ potassium hydroxide solution corresponds to 0·09048 g. of lactic acid. The warming with potassium hydroxide is necessary in order to convert any acid present as anhydride into the acid (in the 75 per cent. acid a quantity of anhydride is present, corresponding to about 1½ per cent. of acid), otherwise the titration would lead to an erroneous result. For this reason it is not advisable to directly titrate a freshly made-up solution of lactic acid with potassium hydroxide solution.

F. Ulzer and H. Seidel[1] give the following method :—10 g. of lactic acid are dissolved in water and made up to 1 litre. 100 c.c. of this solution are taken, and a concentrated solution of potassium hydroxide added until the solution contains 3 g. of potassium hydroxide, when a 5 per cent. potassium permanganate solution is added, with shaking, until the colour of the solution changes from green to violet. The solution is then heated to boiling, which should not discharge the violet coloration, and, after cooling, hydrogen peroxide is added until the coloration is discharged. The solution is then again boiled, filtered, the filter paper washed, and the oxalic acid produced in the reaction precipitated as calcium oxalate after acidifying with acetic acid. The calcium oxalate is ignited and weighed as calcium oxide. From the weight of calcium oxide, the corresponding quantity of oxalic acid and of lactic acid may be calculated.

Methyl Alcohol (Wood Spirit).

$CH_3.OH$.   Molec. wt. 32·03.

Methyl alcohol is a clear, colourless liquid, possessing a characteristic smell. It has a sp. gr. of 0·798, boils at 65°-66°, and is miscible in all proportions with water, alcohol, ether, and with fatty and essential oils.

Tests for Impurities.

Non-volatile Matter. — No appreciable residue should remain on evaporating 30 c.c. of methyl alcohol on the water-bath.

Acetone and Ethyl Alcohol.—On shaking together 50 c.c. of $2N$ sodium hydroxide solution and 5 c.c. of methyl alcohol in a cylinder, then adding 25 c.c. of $2N$ iodine solution, and again shaking, there should be no separation or smell of iodoform. G. Denigès[2] has published a method for detecting traces of acetone, using mercuric sulphate, by means of which he claims that 0·003 per cent. of acetone can be detected.

Empyreumatic Matter.—1 c.c. of methyl alcohol should dissolve in

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[1] *Monatsh.*, 1897, **18**, 138 ; *J. Chem. Soc. Abstr.*, 1897, **72**, 389.
[2] *Merck's Reag.-Verz.*, 1908, p. 56.

10 c.c. of water without turbidity. No coloration or only a faint yellow coloration should be produced on adding 5 c.c. of concentrated sulphuric acid gradually to 5 c.c. of methyl alcohol, the mixture being cooled during the addition.

Chloroform.—No smell of isonitrile should be evolved on heating to boiling 10 c.c. of methyl alcohol with a mixture of 3 drops of aniline and 10 c.c. of alcoholic potash (10 per cent.).

Aldehyde.—On shaking 10 c.c. of methyl alcohol with 10 c.c. of sodium hydroxide solution (1 : 3), the mixture should remain colourless.

Substances oxidised by Permanganate. — The pink coloration produced by the addition of a drop of $N/10$ potassium permanganate solution to 10 c.c. of methyl alcohol should not completely fade away within ten minutes.

In addition to chemically pure methyl alcohol, other qualities come on to the market which only partially satisfy the requirements given above. The examination of wood naphtha is described in the section on "Alcohol, Potable Spirits, and Liqueurs," p. 715.

Quantitative Estimation.

The estimation of methyl alcohol in mixtures of the alcohol and water is effected by means of the specific gravity. A Table of the specific gravities of such mixtures, giving the percentages of methyl alcohol by weight, is included in the section on "Organic Dyes," Vol. II., Part II., p. 894.

In other cases methyl alcohol is generally estimated by determining the amount of methyl iodide produced from a known quantity of the alcohol, a method due originally to Krell, which has been worked out by M. Grodzky and G. Krämer.[1] For this purpose 30 g. of amorphous phosphorus are placed in a small 60 c.c. flask fitted with an upright condenser, and after allowing 10 c.c. of methyl alcohol to drop in from a small separating funnel, 10 c.c. of a solution of 1 part of iodine in 1 part of hydriodic acid (sp. gr. 1·7) are added. After the solution has digested for a short time, the contents of the flask are allowed to cool, the flask connected up with an ordinary condenser, and the contents distilled off on the water-bath, the distillate being collected in a graduated glass cylinder containing some water. When the distillation is ended, the condenser is washed out with water, the distillate well shaken, and the number of cubic centimetres of separated methyl iodide read off at 15°.

The form of this method, as used for the estimation of methyl alcohol in wood naphtha, is described on p. 716.

Quantitative Estimation in presence of Ethyl Alcohol.—For the

[1] *Ber.*, 1874, **7**, 1492.

estimation of methyl alcohol, in presence of ethyl alcohol, the method of T. E. Thorpe and J. Holmes,[1] which depends upon the oxidation of the methyl alcohol to carbon dioxide, is reliable and accurate. The process is described in detail in the section on "Alcohol, Potable Spirits, and Liqueurs," p. 717.

Estimation of Acetone.—G. Krämer's method for estimating acetone in methyl alcohol has been described above as a method for the quantitative estimation of acetone (p. 309).

For the estimation of acetone in methyl alcohol, 1 c.c. of the sample is shaken in a stoppered measuring cylinder with 10 c.c. of $2N$ sodium hydroxide solution, and 5 c.c. of $2N$ iodine solution added. After standing for some time, 10 c.c. of ether are added, the mixture again shaken, the volume of the separated ether layer read off, and an aliquot part, about 5 c.c., withdrawn, allowed to evaporate on a clock-glass, and the residual iodoform dried over sulphuric acid and weighed. 3·94 g. iodoform correspond to 0·58 g. of acetone.

The following volumetric modification of this method is due to J. Messinger[2]:—20 c.c. of potassium hydroxide solution (56 g. to the litre) and 1 c.c. of methyl alcohol are shaken up together in a 250 c.c. stoppered flask, and 20-30 c.c. of $N/5$ iodine solution run in from a burette. The contents of the flask are shaken for about half a minute until the liquid clears, when 20 c.c. of hydrochloric acid (sp. gr. 1·025) and $N/10$ sodium thiosulphate solution, in excess, are added. The solution is then titrated back with $N/5$ iodine solution, using starch solution as indicator.

1 mol. of acetone (58·048 g.) requires 3 mols. of iodine (761·52 g.) for the formation of iodoform, in accordance with the equations :—
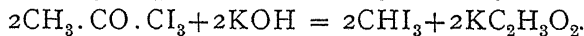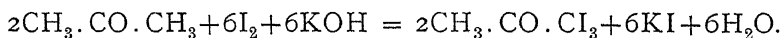
$$2CH_3 . CO . CH_3 + 6I_2 + 6KOH = 2CH_3 . CO . CI_3 + 6KI + 6H_2O.$$
$$2CH_3 . CO . CI_3 + 2KOH = 2CHI_3 + 2KC_2H_3O_2.$$
$$761·52 : 58·048 = I : A$$

$$I = \text{quantity of iodine, } A = \text{quantity of acetone}$$

$$\text{Hence, } A = I . \frac{58·048}{761·52} = 0·07623I.$$

The quantity of acetone (in grams) in 100 c.c. of methyl alcohol is therefore found by multiplying the quantity of iodine used up by 7·623. The percentage content by weight is calculated from the specific gravity of the methyl alcohol.

The following method for the estimation of acetone in methyl alcohol, due to S. J. M. Auld,[3] is based on the formation of bromoform and its subsequent saponification by alcoholic potassium hydroxide. The sample is diluted with water, so that the solution to be tested

[1] *J. Chem. Soc.*, 1904, 85, 1.   [2] *Ber.*, 1888, 21, 3366.
[3] *J. Soc. Chem. Ind.*, 1906, 25, 100.

contains from 0·1-0·2 g. of acetone, and the latter placed in a flask fitted with an upright condenser and dropping funnel. After adding 20-30 c.c. of potassium hydroxide solution (10 per cent.), a solution of bromine (200 g. bromine and 250 g. potassium bromide to a litre of water) is added from the dropping funnel until the mixture has acquired a faint yellow tinge. The whole is then warmed on the water-bath, at about 70°, the bromine solution being added, drop by drop, until a slight coloration remains permanent. The excess of bromine is removed by boiling for a short time with potassium hydroxide solution, and the bromoform then distilled off. The condenser is washed down with alcohol, and 50 c.c. of alcohol and sufficient potassium hydroxide added to produce a distillate containing about 10 per cent. of potassium hydroxide. The bromoform is then saponified by boiling for about three-quarters of an hour, using a reflux condenser, and, when cold, the contents of the flask are neutralised with nitric acid and made up to 500 c.c. with water. The solution is then titrated in the usual way with $N/10$ silver nitrate solution. 239·76 parts of bromine correspond to 58·048 parts of acetone.

Morphine.

$C_{17}H_{19}O_3N \cdot H_2O$.   Molec. wt. 303·18.

Morphine crystallises in colourless needles or prisms which lose their water of crystallisation at 110°-120°, and melt at about 230°. It is only very sparingly soluble in water (about 1 : 5000) and the aqueous solution is lævorotatory; it dissolves in 100 parts of 90 per cent. alcohol, in 50 parts of absolute alcohol, in 100 parts of chloroform, and in 1200 parts of ether. It is practically insoluble in benzene.

It is examined in the same way as morphine hydrochloride. (Cf. *infra.*)

The free base may be estimated volumetrically by treating with an excess of $N/10$ hydrochloric acid, and after adding water, ether, and iodo-eosine as indicator, titrating back with $N/10$ potassium hydroxide. 1 c.c. of $N/10$ hydrochloric acid corresponds to 0·02852 g. of anhydrous morphine, or to 0·03032 g. of $C_{17}H_{19}NO_3 \cdot H_2O$.

Morphine Hydrochloride.

$C_{17}H_{19}O_3N \cdot HCl \cdot 3H_2O$.   Molec. wt. 375·68.

Morphine hydrochloride crystallises in white, silky, non-efflorescent needles, which generally come on to the market compressed into cubes. It is soluble in 25 parts of water and in 50 parts of 90 per cent. alcohol. From the cold, saturated solution the salt is partially thrown

down on the addition of concentrated hydrochloric acid. A deep red coloration is produced on heating a few small crystals for a quarter of an hour in a water-bath with 5 drops of sulphuric acid, allowing to cool, and then adding 1 drop of nitric acid. A mixture of 0·1 g. of morphine hydrochloride and 0·4 g. of cane sugar, added to sulphuric acid, colours the latter red; the coloration is intensified by adding bromine water. On moistening with nitric acid, morphine hydrochloride becomes coloured red. A solution of morphine hydrochloride in sulphuric acid turns brown on the addition of basic bismuth nitrate.

Tests for Impurities.

Inorganic Impurities.—On heating, 0·3 g. of morphine hydrochloride should burn away, leaving not more than 0·5 mg. of residue.

On igniting morphine, there always remains a visible, not insignificant residue, and it is only by weighing that it is possible to ascertain with certainty whether it is negligible.

Free Hydrochloric Acid.—The aqueous solution should react neutral with litmus paper.

Sugar and Organic Impurities.—Morphine hydrochloride should dissolve in sulphuric acid, producing a colourless or, at most, a faint pink-coloured solution.

Foreign Alkaloids.—On adding a drop of potassium carbonate solution (1 : 3) to 5 c.c. of an aqueous solution of morphine hydrochloride (1 : 30), a pure white, crystalline separation takes place immediately or in the course of a few seconds, which should remain colourless in contact with air, and on shaking up with chloroform the latter should not be reddened (apomorphine). Instead of potassium carbonate, potassium bichromate may also be used, which brings about an immediate oxidation. On shaking with chloroform, the latter is immediately turned red if apomorphine be present. The addition of a drop of ammonia to 5 c.c. of an aqueous solution (1 : 30) produces an immediate white, crystalline precipitate, which should dissolve readily in sodium hydroxide solution, and slowly in ammonia or lime water, giving colourless solutions. On shaking up the sodium hydroxide solution with ether, the clear ethereal extract should yield no appreciable residue on evaporation. (A residue points to the probable presence of narcotine.)

Water.—On drying 1 g. of morphine hydrochloride at 100° till constant, at least 0·856 g. of residue should remain.

The methods for the examination of the two most important derivatives of morphine, viz., codeïne and dionine, are appended.

Codeïne (Methyl Morphine).

$$C_{17}H_{17}ON(OH)(OCH_3) + H_2O. \quad \text{Molec. wt. } 317 \cdot 19.$$
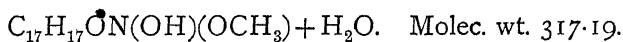
Codeïne forms colourless crystals which are soluble in 80 parts of cold, and in 17 parts of boiling water. It is readily soluble in alcohol, ether, and chloroform. On drying at 100°, it loses 5·68 per cent. in weight. Anhydrous codeïne melts at 153°. The free codeïne base may be estimated volumetrically in the same way as morphine (p. 365). 1 c.c. of $N/10$ hydrochloric acid corresponds to 0·03172 g. of codeïne + H_2O.

The salt of codeïne which finds the widest application is the phosphate, $C_{17}H_{17}ON(OH)(OCH_3) . H_3PO_4 + 2H_2O$. Molec. wt. 433·234. It crystallises in fine white needles, soluble in 3·5 parts of water, and less soluble in alcohol. Its aqueous solution reddens litmus paper. Codeïne phosphate dissolves in sulphuric acid to a colourless solution, sometimes exhibiting a transitory pale red coloration; on adding a drop of ferric chloride, the mixture turns blue on warming; when cold, a drop of nitric acid changes the blue coloration to a deep red.

Tests for Impurities.

Sulphuric and Hydrochloric Acids.—An aqueous solution (1 : 20), acidified with nitric acid, should show no change with silver nitrate solution, and barium nitrate solution should produce no immediate turbidity.

Morphine.—A solution of a small piece of potassium ferricyanide in 10 c.c. of water, to which is added a drop of ferric chloride, should not be turned blue immediately on the addition of 1 c.c. of an aqueous solution of codeïne phosphate (1 : 100).

Water.—Codeïne phosphate should not lose more than 8·5 per cent. in weight on drying at 100°.

Quantitative Estimation.

This may be carried out by dissolving a weighed quantity of the salt in water, making alkaline with sodium carbonate solution, extracting with ether, and titrating the ethereal codeïne solution obtained with $N/10$ hydrochloric acid, using iodo-eosine as indicator.

Dionine (Ethyl Morphine Hydrochloride).

$$C_{17}H_{18}O_2N(OC_2H_5)HCl + 2H_2O. \quad \text{Molec. wt. } 385 \cdot 69.$$
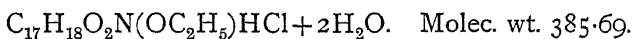
Dionine is a white, crystalline powder consisting of fine small needles soluble in 12 parts of water and in 25 parts of alcohol (of about 85 per cent. by weight). The solution in water reacts neutral

with litmus paper.   On adding a solution of iodine in potassium iodide to the aqueous solution (1 : 100), a light brown precipitate is thrown down.   0·01 g. of dionine dissolves in 10 c.c. of sulphuric acid (sp. gr. 1·84) with evolution of hydrochloric acid, a clear, colourless solution resulting which, when warmed with a drop of ferric chloride solution, first turns green, then deep blue, and on the further addition of 2-3 drops of nitric acid, the colour changes to deep red.

Tests for Impurities.

Codeïne.—1 or 2 drops of ammonia (10 per cent. NH_3) added to a solution of 0·1 g. of dionine in 1 c.c. of water, produces a white precipitate which is not dissolved on the further addition of 10-15 drops of ammonia.   (Under similar conditions codeïne goes readily into solution.)

Morphine.—A solution of a small crystal of potassium ferricyanide in 10 c.c. of water, to which a drop of ferric chloride solution is added, should not turn immediately blue, but should only very slowly develop a bluish-green coloration on the addition of 1 c.c. of an aqueous solution of dionine (1 : 100).   (Morphine gives an immediate deep blue coloration.)

Inorganic Impurities.—Not more than 0·5 mg. of residue should remain on igniting 1 g. of dionine.

Water.—On drying at 100°, dionine should not lose more than 9·5 per cent. in weight.

Quantitative Estimation.

The dionine (0·25 g.) is dissolved in 50 c.c. of absolute alcohol in a glass-stoppered flask, and the solution titrated with $N/10$ potassium hydroxide, using Poirrier's blue as indicator (*cf.* Quinine, p. 381).   1 c.c. of $N/10$ potassium hydroxide corresponds to 0·0386 g. of dionine.

α-Naphthol.

$C_{10}H_7 . OH.$ Molec. wt. 144·06.

α-Naphthol crystallises in colourless needles possessing a phenol-like smell.   It melts at 97° and boils at 280°.   It is sparingly soluble in water, but readily in alcohol, ether, benzene, and chloroform.

Qualitative Tests.

1. An aqueous solution of α-naphthol gives a violet coloration with calcium hypochlorite solution, and also with a solution of iodine in potassium iodide on the addition of an excess of sodium hydroxide solution.

2. Ammonia produces a blue fluorescence when added to an aqueous solution.

3. An alcoholic solution (1:5) gives a violet coloration with ferric chloride; the coloration disappears on standing for some time.

4. On melting 0·5 g. of α-naphthol with 12 g. of chloral hydrate for ten minutes in a boiling water-bath, the mass turns red, and dissolves in alcohol, producing a red coloration.

5. If 0·1 g. of vanillin be dissolved in 2 c.c. of sulphuric acid, and then 0·1 g. of α-naphthol added, a very stable red coloration is produced after shaking for some time.[1]

Tests for Impurities.

Inorganic Acids.—On shaking 1 g. of α-naphthol with 100 c.c. of water, the filtrate should not redden blue litmus paper.

Organic Impurities insoluble in Sodium Hydroxide.—1 g. of α-naphthol should dissolve completely to a clear solution in 5 c.c. of sodium hydroxide solution of sp. gr. 1·168-1·172 and 5 c.c. of water.

Inorganic Matter.—No appreciable residue should remain on igniting 1 g. of α-naphthol.

Quantitative Estimation.

The acidimetric method for the estimation of α-naphthol is described in the section on "Organic Dyes," Vol. II., Part II., p. 882.

β-Naphthol.

$C_{10}H_7 . OH$.   Molec. wt. 144·06.

β-Naphthol forms colourless, glistening, odourless, rhombic crystals, which melt at 128°, and boil at 285°-290° with slight decomposition.

Qualitative Tests.

1. Calcium hypochlorite solution gives a yellow coloration with an aqueous solution of β-naphthol; the coloration disappears if a slight excess of the reagent be added. β-Naphthol gives no coloration with a solution of iodine in potassium iodide containing excess of sodium hydroxide.

2. Ammonia produces a violet fluorescence when added to an aqueous solution.

3. An alcoholic solution (1:5) gives a stable green coloration with ferric chloride.

4. On melting 0·5 g. of β-naphthol with 12 g. of chloral hydrate for ten minutes in a boiling water-bath, the mass turns a deep blue, and dissolves in alcohol, producing a blue coloration.

[1] For other colour reactions, cf. *Merck's Reag.-Verz.*, 1908, p. 297.

5. If 0·1 g. of vanillin be dissolved in 2 c.c. of sulphuric acid, and then 0·1 g. of β-naphthol added, the solution turns a chlorophyll-green colour.

Tests for Impurities.

α-Naphthol.—If 1 g. of β-naphthol be dissolved in 100 c.c. of boiling water, and the solution cooled and filtered, the filtrate should not show a violet coloration on the addition of excess of calcium hypochlorite solution. Other methods for the detection of α-naphthol, and for the differentiation of the two isomers, are described in the section on "Organic Dyes," Vol. II., Part II., pp. 881 *et seq.*

Naphthalene.—1 g. of β-naphthol should dissolve completely, leaving no residue, in 50 c.c. of ammonium hydroxide (sp. gr. 0·96).

Organic Impurities.—The above ammoniacal solution should not have a brownish colour, but should only be pale yellow.

Organic Acids.—On shaking 1 g. of β-naphthol with 100 c.c. of water and filtering, the filtrate should not redden blue litmus paper.

Quantitative Estimation.

F. W. Küster's method for the acidimetric estimation of β-naphthol by means of its picric acid compound, is described in the section on "Organic Dyes," Vol. II., Part II., p. 882.

Oxalic Acid.

$$C_2H_2O_4 \cdot 2H_2O. \quad \text{Molec. wt. } 126·05.$$
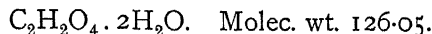
Oxalic acid crystallises in colourless, monoclinic crystals, which should show no signs of efflorescence. It dissolves in 10 parts of water at 15°, in about 3 parts of boiling water, in 2·5 parts of alcohol at 15°, in 1·8 parts of boiling alcohol, and in about 100 parts of ether. The hydrated acid heated in a capillary tube melts in its water of crystallisation at 98°; the anhydrous acid melts at 187°. On heating oxalic acid with sulphuric acid, carbon monoxide and carbon dioxide are evolved. Calcium chloride, added to an aqueous solution containing excess of ammonia, produces a white precipitate, insoluble in acetic, but soluble in hydrochloric acid.

Tests for Impurities.

Inorganic Matter.—No appreciable residue should remain on igniting 3 g. of oxalic acid.

Ammonium Compounds.—On treating 2·5 g. of oxalic acid with 5 g. of potassium hydroxide dissolved in 30 c.c. of water, and then adding

15 drops of Nessler's reagent to the solution, only a pale yellowish coloration, and not a reddish-brown coloration should result.

Heavy Metals.—An aqueous solution (1 : 10) should be perfectly clear. 30 c.c. of this solution should show no reaction on the addition of sulphuretted hydrogen water, or on the subsequent addition of ammonia, till alkaline.

Chlorides.—At most, only a faint opalescence should be produced on adding silver nitrate solution to a solution of 5 g. of oxalic acid in 50 c.c. of water acidified with 15 c.c. of nitric acid.

Sulphuric Acid.—No turbidity or precipitate should be produced on warming an aqueous solution (5 : 100), acidified with hydrochloric acid, with barium chloride solution within fifteen hours.

Nitric Acid.—On carefully pouring a 10 per cent. solution of oxalic acid on to 10 c.c. of a solution of diphenylamine in sulphuric acid, no blue ring should be visible at the junction of the two layers of liquid.

Quantitative Estimation.

1 g. of oxalic acid is dissolved in water and made up to 100 c.c., 25 c.c. of which are titrated hot with $N/5$ potassium hydroxide solution, using phenolphthalein as indicator. 1 c.c. of $N/5$ potassium hydroxide corresponds to 0·012605 g. of crystallised oxalic acid.

As an alternative method 25 c.c. of the above aqueous solution (1 : 100) are titrated with $N/10$ potassium permanganate solution after adding 6-8 c.c. of concentrated sulphuric acid, and warming to about 60°. 1 c.c. of $N/10$ potassium permanganate = 0·0063025 g. of crystallised oxalic acid.

A Table of the specific gravity of aqueous solutions of oxalic acid is given in the section on "Organic Dyes," Vol. II., Part II., p. 898.

Paraldehyde.

$(CH_3COH)_3$. Molec. wt. 132·10.

Paraldehyde is a clear, colourless liquid with a peculiar, not irritating smell. It has a sp. gr. of 0·997-1·000, boils at 123°-125° solidifies below 10°, and melts at 10°·5. According to W. Squire,[1] absolutely pure paraldehyde melts at 11°·7. Paraldehyde is readily soluble in alcohol, ether, benzene, chloroform, and petroleum spirit; it dissolves in 10 parts of water. A cold, saturated solution becomes turbid on warming.

Tests for Impurities.

Inorganic Matter.—20 c.c. of paraldehyde should volatilise completely on hearing, leaving no residue.

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[1] *Chem. and Drug.*, 1890, **37**, 852.

Hydrochloric and Sulphuric Acids.—Neither silver nitrate nor barium nitrate solution should produce any precipitate in an aqueous solution (1 : 10) acidified with nitric acid.

Acetic and Valeric Acids.—10 c.c. of paraldehyde are dissolved in 50 c.c. of alcohol, and phenolphthalein added ; not more than 0.5 c.c. of $N/1$ potassium hydroxide should be required to produce the pink coloration.

Alcohol.—The presence of alcohol is indicated by a too low specific gravity, melting point, and boiling point. On shaking up 20 c.c. of paraldehyde with 20 c.c. of a saturated solution of calcium chloride, the volume of the latter should show no increase.

Water.—Paraldehyde should dissolve to a perfectly clear solution in an equal volume of official paraffin oil (liquid paraffin).

Aldehyde.—On shaking up 10 c.c. of paraldehyde with 10 c.c. of 5 per cent. potassium hydroxide solution, the latter should show no yellow or brown coloration within half an hour.

Valeraldehyde.—No disagreeable smelling residue should remain on evaporating 10 c.c. of paraldehyde down on the water-bath.

Amyl Alcohol.—The aqueous solution (1 : 10) should be perfectly clear and contain no oily drops.

Phenacetine.

$$C_6H_4{<}^{OC_2H_5(1)}_{NH . COCH_3(4)} .\qquad \text{Molec. wt. } 179 \cdot 11.$$
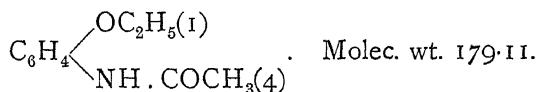
Phenacetine forms colourless, odourless, and tasteless, small, leafy crystals, which melt at 135°. It dissolves in 1400 parts of water at 15°, in 70 parts of boiling water, and in 16 parts of alcohol.

On boiling 1 g. of phenacetine with 10 c.c. of hydrochloric acid for about a minute, diluting with 100 c.c. of water, allowing to cool and filtering, the filtrate gradually assumes an intense red colour on adding 1-2 c.c. of chromic acid solution (3 : 100).[1]

Tests for Impurities.

Inorganic Matter.—Not more than 0.5 mg. of residue should remain on igniting 0.5 g. of phenacetine.

Organic Impurities.—No brown coloration or carbonisation should be produced on dissolving 0.5 g. of phenacetine in 10 c.c. of sulphuric acid.

Acetanilide.—On heating 0.5 g. of phenacetine with 8 c.c. of water to boiling, allowing to cool and filtering, the filtrate should show no reaction on boiling with potassium nitrite and dilute nitric acid, and

[1] For identifying reactions for phenacetine, cf. *Merck's Reag.-Verz.*, 1908, p. 298.

again boiling with nitric acid containing nitrous acid. According to J. Schroeder,[1] 2 per cent. of acetanilide may be thus detected by the production of a red coloration.

On boiling 0·3 g. of phenacetine for about one minute with 3 c.c. of 25 per cent. hydrochloric acid, diluting with 30 c.c. of water and filtering, 10 drops of 3 per cent. chromic acid solution should produce a stable ruby-red but not a green coloration.[2]

Phenol.—If 0·1 g. of phenacetine be dissolved in 10 c.c. of hot water, the solution allowed to cool and then filtered, the filtrate should show no turbidity on adding excess of bromine water.

Free Acids or Bases.—A 5 per cent. alcoholic solution of phenacetine should give no reaction with either red or blue litmus paper.

Para-Phenetidene.—On stirring 1 g. of phenacetine into 5 g. of molten chloral hydrate, a clear and colourless melt should result. The mixture should not be heated in the steam-bath for longer than two to three minutes, otherwise pure phenacetine turns a rose-red colour. In the presence of *p*-phenetidene the melt becomes coloured violet.[3]

As an alternative test, 0·5 g. of phenacetine is dissolved by warming with 2 c.c. of alcohol, and 5 c.c. of iodine in potassium iodide solution (0·05 iodine : 1000) added. The solidified mass of separated phenacetine is heated to boiling till dissolved. In the presence of traces of *p*-phenetidene the solution turns rose-red. The colour is more marked if the phenacetine be separated out a second time.[4]

Ortho- and Diamino-Compounds.—It is not usually necessary to test for these, since the commercial product is practically always free from such compounds as impurities.[5]

Para-Chloracetanilide.—An adulteration with this substance is indicated by a low melting point. The chlorine may be detected by igniting the phenacetine with calcium carbonate in a similar manner to that by which benzoic acid is tested for chlorobenzoic acid[6] (p. 321).

Quantitative Estimation.

A method for the quantitative estimation of phenacetine in mixtures has been worked out by J. L. Turner and C. E. Vanderkleed.[7]

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[1] *Z. anal. Chem.*, 1889, **28**, 376.   [2] *Union pharmac.*, 1905, p. 484.

[3] Reuter, *Pharm. Zeit.*, **36**, 185 ; *cf.* also *Pharm. Zentralh.*, **32**, 313.

[4] Goldmann, *Pharm. Zeit.*, **36**, 208.

[5] A method of testing for these compounds is given in *Pharm. Zentralh.*, **31**, 65, and **32**, 313.

[6] *Cf.* Sudd, *Apoth. Zeit.*, 1906, p. 236 ; C. Mannich, *Ber. Pharm.*, 1906, p. 57 ; *J. Soc. Chem. Ind.*, 1906, **25**, 495.

[7] *Amer. J. Pharm.*, April 1907 ; *J. Soc. Chem. Ind.*, 1907, **26**, 486.

Phenyldimethylpyrazolone (Antipyrine).

$$C_6H_5 . N \begin{array}{c} N(CH_3) . C—CH_3 \\ \| \\ CO——CH \end{array} . \quad \text{Molec. wt. } 188·12.$$
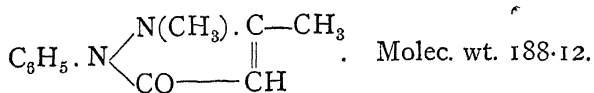
Antipyrine crystallises in colourless plates possessing a slightly bitter taste. Melting point 110°-112°. It dissolves in 1 part of water, 1·5 parts of chloroform, and in 80 parts of ether. A solution of tannic acid added to an aqueous solution of antipyrine (1 : 100) gives a voluminous white precipitate. 2 drops of fuming nitric acid added to 2 c.c. of an aqueous solution produce a green coloration, and after boiling, the addition of a further drop of the acid causes a red coloration. A drop of ferric chloride solution added to 2 c.c. of an aqueous solution (1 : 1000) produces a deep red coloration, which changes to a bright yellow on adding 10 drops of sulphuric acid.[1]

Tests for Impurities.

The aqueous solution of antipyrine (1 : 1) should be clear and colourless. It should react neutral and remain unchanged on adding sulphuretted hydrogen water. A solution of 1 g. of the preparation in 5 c.c. of water should show no reaction on heating to boiling with 3 drops of silver nitrate solution. No appreciable residue should remain on igniting 0·1 g. of antipyrine

Quantitative Estimation.[2]

This may be carried out by means of iodine either volumetrically, the antipyrine being converted into the periodide of its hydriodide, $C_{11}H_{12}N_2O . HI . I_2$, and the excess of iodine being titrated back with sodium thiosulphate, or gravimetrically by the method of the French Codex, in which the antipyrine is precipitated and weighed as the difficultly soluble iodo-antipyrine, which contains 70 per cent. of iodine.[3]

Phenylhydrazine.

$$C_6H_5 . NH . NH_2. \quad \text{Molec. wt. } 108·08.$$
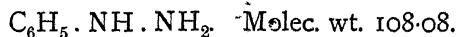
Phenylhydrazine is a colourless or pale yellow, slightly refractive liquid, which boils at 243°, and on cooling solidifies in monoclinic plates which melt at 19°. Phenylhydrazine forms a crystalline hydrate with

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[1] For other identifying reactions, cf. *Merck's Reag.-Verz.*, 1908, p. 290; also G. Lander and H. Winter, *Analyst*, 1913, **38**, 97.

[2] *Cf.* C. Kippenberger, *Z. anal. Chem.*, 1896, **35**, 675; *J. Soc. Chem. Ind.*, 1896, **15**, 266. J. Bougault, *J. Pharm. Chim.*, 1900, **11**, 97; *J. Soc. Chem. Ind.*, 1900, **19**, 269.

[3] *Cf.* C. Astre, *J. Pharm. Chim.*, 1912, **6**, 211; *J. Soc. Chem. Ind.*, 1912, **31**, 898.

water ($2C_6H_5 . N_2H_3 . + H_2O$), which melts at 25°. It is but sparingly soluble in cold water, more so in hot, and very readily in alcohol and ether. It reduces Fehling's solution in the cold. If an aqueous or alcoholic solution of phenylhydrazine be heated for a short time with a few drops of an aqueous solution of trimethylamine, and then a few drops of a solution of sodium nitroprusside added, an intense cherry-red coloration is produced. On warming 5 c.c. of a solution of 1 g. of phenylhydrazine and 2 g. of sodium acetate in 15 c.c. of water and 1·5 g. of hydrochloric acid (sp. gr. 1·124) with 10 c.c. of grape sugar solution (1 : 100) in a boiling water-bath, fine yellow needles of phenyl glucosazone begin to separate in about ten minutes; an additional separation takes place on further heating.

Tests for Impurities.

A clear solution should result on dissolving 2 g. of phenylhydrazine in 20 c.c. of 5 per cent. acetic acid.

Quantitative Estimation.

A method for the quantitative estimation of phenylhydrazine has been worked out by H. Causse.[1] It is based on the reduction of arsenic acid by means of phenylhydrazine to arsenious acid with formation of nitrogen and phenol, according to the following equation :—

$$As_2O_5 + C_6H_5NH . NH_2 = N_2 + C_6H_5OH + As_2O_3 + H_2O.$$
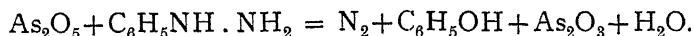
The estimation is carried out as follows :—0·2 g. of phenylhydrazine and 60 c.c. of arsenic acid solution (125 g. of pure arsenic acid are dissolved by heating on the water-bath in 450 c.c. of water and 150 c.c. of pure, concentrated hydrochloric acid; when cold, the solution is filtered, and made up to 1000 c.c. with glacial acetic acid) are gently heated in a round-bottomed 500 c.c. flask, fitted with upright condenser, until the evolution of gas has subsided; the contents of the flask are then boiled for about forty minutes. When cold, 200 c.c. of water are added, and the solution made faintly alkaline (until phenolphthalein just turns pink) with a solution of sodium hydroxide containing 200 g. of sodium hydroxide to the litre. The solution is then made just acid with hydrochloric acid, 60 c.c. of a cold, saturated solution of sodium bicarbonate added, and the arsenious acid finally titrated with $N/10$ iodine solution. 1 c.c. of the latter corresponds to 0·002702 g. of phenylhydrazine.

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[1] *Comptes rend.*, 1897, 125, 712 ; *J. Soc. Chem. Ind.*, 1898, 17, 76.

Phthalic Acid.

$$C_6H_4 \begin{cases} COOH(1) \\ COOH(2) \end{cases}$$ Molec. wt. 166·05.
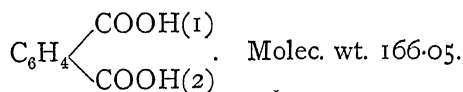
Phthalic acid crystallises in small, colourless plates or prisms melting at 213° and soluble in 200 parts of water, 10 parts of alcohol, and 145 parts of ether; it is only very sparingly soluble in chloroform, and is insoluble in benzene and in petroleum spirit. On heating to about 130°, it is gradually converted into phthalic anhydride and water.

Phthalic Anhydride.

$$C_6H_4 \begin{cases} CO \\ CO \end{cases} O.$$ Molec. wt. 148·032.
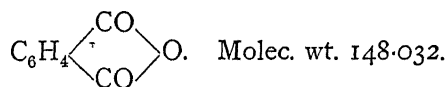
Phthalic anhydride crystallises in long, colourless needles which melt at 128° and boil at 277°. It dissolves in boiling water forming phthalic acid, and in alcohol, ether, benzene, and chloroform, whilst it is only sparingly soluble in petroleum spirit. The anhydride commences to sublime below its melting point.

A dilute, aqueous solution of phthalic acid gives a white precipitate (even at a dilution of 1 : 10,000) with lead acetate, the precipitate being readily dissolved by nitric acid, but only soluble with difficulty in excess of acetic acid. On melting phthalic anhydride with resorcinol in a test tube, and dissolving the cold melt in alkali, the alkaline solution, when poured into a large volume of water, produces a highly fluorescent solution due to the formation of fluorescein.

Tests for Impurities.

Inorganic Matter.—Not more than 0·5 mg. of residue should be left on igniting 1 g. of phthalic acid.

Hydrochloric Acid.—Only a faint opalescence should be produced on adding silver nitrate solution to a solution of 1 g. of phthalic acid in 25 c.c. of boiling water.

Chlorine Compounds.—0·5 g. of phthalic acid is mixed with 1 g. of calcium carbonate free from chloride, moistened with water, dried, and ignited. On dissolving the ignited residue to a volume of 20 c.c. in nitric acid and water, and adding silver nitrate solution, only a faint opalescent turbidity should be produced.

Benzoic Acid.—1 g. of phthalic acid is shaken up with 20 c.c. of benzene and filtered. No residue should be left on evaporating the filtrate. Since the anhydride is soluble in benzene it should first be

converted into the acid by dissolving in hot water, evaporating and drying at 100°.

For technical purposes, *e.g.* in the colour industry, it suffices if the anhydride melts at 128°, is soluble in benzene, and volatilises without leaving any residue. Dichlorophthalic acid and tetrachlorophthalic acid, used in the preparation of eosin dyes, melt at 183°-185° and 250° respectively, the latter forming an anhydride.

1 : 3 Phthalic Acid (Isophthalic acid) crystallises in long, fine needles which melt above 300°, and dissolve in about 4000 parts of water, but are more soluble in alcohol. It is insoluble in benzene, chloroform, and petroleum spirit.

1 : 4 Phthalic Acid (Terephthalic acid) crystallises in small, needle-like crystals, which sublime on heating without melting. It is insoluble in benzene and petroleum spirit, and but very sparingly soluble in water, ether, and chloroform.

Quantitative Estimation.

1 g. of phthalic acid or anhydride is dissolved in 20 c.c. of $N/1$ sodium hydroxide and 20 c.c. of water, and then titrated with $N/1$ hydrochloric acid. 1 c.c. of $N/1$ sodium hydroxide, used in neutralisation, corresponds to 0·08302 g. of phthalic acid, or to 0·07402 g. of phthalic anhydride.

Pyrogallol.

$$C_6H_3(OH)_3 \ [1 : 2 : 3]. \quad \text{Molec. wt. } 126·05.$$

Pyrogallol crystallises in colourless, glistening needles or small plates which melt at 131°. It dissolves in 1·7 parts of water, in 1·5 parts of alcohol, in 1·5 parts of ether, and sparingly in benzene, chloroform, and carbon bisulphide. The aqueous solution reacts faintly acid. An aqueous solution is coloured blue by a freshly prepared solution of ferrous sulphate, brownish-red by ferric chloride, and is blackened by silver nitrate solution.[1]

Tests for Impurities.

Inorganic Matter.—No appreciable residue should be left on igniting 1 g. of pyrogallol.

Gallic Acid.—2 g. of pyrogallol should dissolve to a perfectly clear solution in 5 c.c. of ether (sp. gr. 0·72). 0·1 per cent. of gallic acid is thus readily detected, either a turbid solution being produced or a small amount of crystalline residue remaining undissolved.

[1] For identifying and colour reactions, cf. *Merck's Reag.-Verz.*, 1908, p. 299.

Quinine.

$C_{20}H_{24}O_2N_2$.   Molec. wt. 324·21.
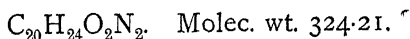
Pure quinine comes into commerce chiefly as the hydrate $C_{20}H_{24}O_2N_2 + 3H_2O$. It is a white, crystalline, bitter-tasting powder which readily effloresces in the air, but which only loses its water of crystallisation completely by prolonged drying at 100°. The hydrate melts at 57°.

Anhydrous quinine, obtained as fine, silky needles by crystallisation from dilute alcohol, melts at 174°·6. It is tested for purity in the same manner as quinine sulphate, being first converted into the latter.

The free base may be estimated volumetrically, using lacmoid as indicator. 1 c.c. of $N/10$ hydrochloric acid corresponds to 0·03242 g. of quinine (anhydrous), or to 0·03783 g. of quinine + 3H2O.[1]

Quinine Sulphate.

$(C_{20}H_{24}O_2N_2)_2 . H_2SO_4 + 8H_2O$.   Molec. wt. 890·64.
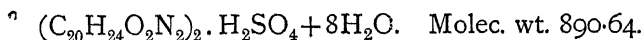
The sulphate forms fine white needles with a bitter taste, and is soluble in 800 parts of water at 15°, in 100 parts of alcohol, in 40 parts of glycerol, and is practically insoluble in chloroform and in ether; it dissolves in 25 parts of boiling water and in 6 parts of boiling alcohol.

A cold, saturated solution of quinine sulphate shows no fluorescence, but does so on the addition of sulphuric acid. A green coloration is produced on mixing 10 c.c. of an aqueous solution with 2 c.c. of chlorine water and adding excess of ammonia.[2]

Tests for Impurities.

Inorganic and Organic Matter.—Not more than 0·5 mg. of ash should remain on igniting 1 g. of quinine sulphate. The salt should colour but very slightly on moistening with nitric or with sulphuric acid. On dissolving 1 g. of quinine sulphate in 7 c.c. of a mixture of 2 vols. of chloroform and 1 vol. of absolute alcohol at 40°-50°, a clear solution should result, showing no turbidity on cooling.

Acid Quinine Sulphate.—The cold, saturated, aqueous solution should react either neutral or faintly alkaline with litmus paper.

Quinine Hydrochloride.—The cold, saturated, aqueous solution should remain unchanged on the addition of silver nitrate solution.

Salicylic Acid.—Ferric chloride solution should not produce a violet coloration with a cold, saturated, aqueous solution.

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[1] Cf. *Z. angew. Chem.*, 1903, **16**, 449 and 468.

[2] For identifying reactions, cf. *Merck's Reag.-Verz.*, 1908, p. 291, and *Z. angew. Chem.*, 1903, **16**, 477.

Foreign allied Alkaloids.—A test of a general character for the detection of other cinchona alkaloids in quinine, known as the "ammonia test," has been adopted by most of the pharmacopœias, other than the British. This test is based on a method originally proposed by Kerner,[1] and is carried out as follows :—20 c.c. of water are poured on to 2 g. of quinine sulphate completely effloresced at 40°-50°, the mixture frequently shaken, and heated for half an hour in a water-bath at 60°-65°. It is then cooled to 15° and allowed to stand at this temperature, with frequent shaking, for two hours, when it is poured on to a dry piece of linen; as much liquid as possible is squeezed out of the solid matter, and the liquid so obtained filtered. Ammonia (at 15° and of sp. gr. 0·96) is then gradually added to 5 c.c. of the filtrate at 15° until the precipitate at first produced redissolves. The volume of ammonia that should be required for this purpose varies according to the different foreign pharmacopœias; in Germany, for example, it is fixed at 4·0 c.c. F. Tutin,[2] who has conducted a series of careful tests on this reaction, found that the minimum amount of 10 per cent. ammonia that will yield a clear solution at 15° with 5 c.c. of a solution of pure quinine sulphate, saturated at 15°, is 4·4 c.c.; he therefore concludes that it is impossible to meet the requirements of the German Pharmacopœia, and regards a minimum of 6 c.c. as reasonable. This test is also misleading, because any basicity of the salt will have the same effect as impurities, and, further, the presence of small quantities of inorganic salts influences the result. Tutin accordingly regards the test as of value only in the case of normal quinine sulphate; specific tests for cinchonidine and cinchonine are, in his opinion, preferable to the "ammonia test."

Cinchonidine and Cinchonine.—The following test, which depends on the fact that both cinchonidine and cinchonine are less soluble than quinine in ether, is prescribed by the British Pharmacopœia :—4 g. of quinine sulphate are dissolved in 120 c.c. of boiling water, and the solution allowed to cool down with frequent stirring. The separated quinine sulphate is then filtered off, the filtrate evaporated down to 10 c.c., poured into a small, stoppered flask and shaken, when cold, with 10 c.c. of ether and 5 c.c. of ammonia (sp. gr. 0·959). After standing for twenty-four hours in a cool place, the separated crystals of cinchonidine and of cinchonine together with some quinine are collected on a weighed filter paper, washed with a little ether, and dried at 100°. Their weight should not exceed 0·12 g. F. Tutin[3] states that the test is more delicate if ether of sp. gr. 0·720-0·722 (Aether purificatus) be used for the test instead of ether of sp. gr. 0·735.[4]

[1] *Arch. Pharm.*, 1881, 16, 186.   [2] *Pharm. J.*, 1909, 83, 600.   [3] *Ibid.*
[4] *Cf.* B. H. Paul, *Chem. and Drug.*, 1904, 65, 428, and D. Howard, *ibid.*, 1904, 65, 475.

The following alternative test can also be employed:—0.7 g. of quinine sulphate is treated in a large test tube with 20 drops of dilute hydrochloric acid and 7 c.c. of water, then 7 c.c. of crystallisable thiophene-free benzene added, and the mixture heated in a water-bath to 60°-70°. After adding 3 c.c. of ammonia, the mixture is well shaken, poured into a small separating funnel, and the aqueous layer run off after it has completely separated. The benzene solution is allowed to stand for about half an hour to allow the quinine to crystallise out, when it is filtered through a dry filter paper and the filtrate allowed to stand for a further length of time for further crystallisation to take place. If the quinine sulphate under examination contains 1 per cent. of cinchonidine it is possible in three to four hours to recognise feathery groups of small needles along with the quinine (rhombic crystals) which has crystallised out; it is advisable to use a lens to distinguish the two forms of crystals. If more than 1 per cent. of cinchonidine be present, the separation of the needles is more rapid and abundant (with 5 per cent. in about half an hour), whilst with less than 1 per cent. the separation requires several days with slow evaporation of the solution. To avoid error in conclusions, the crystals must be observed and recognised in the liquid, since crystals are formed in the upper parts of the test tube owing to the evaporation of the benzene.[1]

Quinidine.—The following test is that prescribed by the British Pharmacopœia:—1 g. of quinine sulphate is dissolved in 30 c.c. of boiling water, allowed to cool, and filtered. Potassium iodide solution is added to the filtrate, and to avoid the separation of amorphous hydriodides a little 90 per cent. alcohol is also added. Either no crystalline separation of quinidine hydriodide, or only a very small separation, should take place. In the latter case the crystals are collected on a small filter paper, washed with a little water, dried, and weighed. The weight corresponds approximately to the amount of quinidine sulphate in 1 g. of quinine sulphate.

Water.—According to the British Pharmacopœia, 2.5 g. of quinine sulphate on drying at 100° should lose 0.38 g. of water. Details for this estimation are given below under quinine hydrochloride.

Quinine Hydrochloride.

$$C_{20}H_{24}O_2N_2 . HCl + 2H_2O. \quad \text{Molec. wt. 396.71.}$$
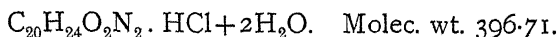
Next to the sulphate this is the most important and most used salt of quinine. It crystallises in white needles frequently united together in tufts, and dissolves in 34 parts of water at 15° and in 3 parts of alcohol. Its solutions are not fluorescent.

[1] Wood and Barret, *Chem. News*, 1883, 48, 3.

Tests for Impurities.

Inorganic Matter.—This test is the same as in the case of the sulphate.

Acid Quinine Hydrochloride.—The same test as in the case of the sulphate. (The solution of the commercial product generally reacts faintly alkaline with litmus paper.)

Quinine Sulphate.—Barium chloride solution should only produce a very faint turbidity with an aqueous solution of the hydrochloride (1 : 50).

Barium Chloride.—Sulphuric acid should show no reaction with an aqueous solution (1 : 50).

Water.—Quinine hydrochloride, on drying at 100°, should not lose more than 9·1 per cent. in weight. The content of water of crystallisation in quinine hydrochloride may be more quickly arrived at volumetrically in the following manner:—To 100 c.c. of absolute alcohol and a few drops of a 1 per cent. aqueous solution of Poirrier's blue in a 150 c.c. glass-stoppered flask, $N/5$ potassium hydroxide is added, drop by drop, until the blue colour of the solution changes to red, and until on shaking in the closed flask there is no return to the blue colour. 1 g. of quinine hydrochloride is then added, which causes a return of the blue colour. On adding 12·6 c.c. of $N/5$ potassium hydroxide, the solution should not change to red if the preparation does not contain more than 9 per cent. of water. If necessary, the titration is continued until a red coloration is produced, in order to determine how much the salt under examination has effloresced. After each addition of potassium hydroxide the flask must be closed, otherwise errors may arise through the action of the carbon dioxide in the air.

Poirrier's blue is a very sensitive indicator to acids, which makes it possible to estimate the mineral acid combined with quinine by titration with alkali in the same way as if it were a free acid.[1]

If 1 g. of quinine sulphate be used under the above conditions, a turbid liquid is produced in which, however, the changes of colour may be equally well recognised. When using a sulphate containing the correct amount of water, the change of colour should not be produced with less than 11·2 c.c. of $N/5$ potassium hydroxide.

Foreign allied Alkaloids.—2 g. of quinine hydrochloride are dissolved in a porcelain dish in 20 c.c. of water at 60°, 1 g. of powdered non-effloresced sodium sulphate added, and the mixture well ground up together with a pestle. When cold, the dish is placed in water at 15° and allowed to stand at this temperature for half an hour, when the mixture is filtered through a dry 7 cm. filter paper, and 5 c.c. of the filtrate tested by one of the methods given for the sulphate.

[1] Cf. *Z. angew. Chem.*, 1903, **16,** 469.

Other quinine salts are tested in a similar manner to the sulphate or hydrochloride, and must be treated according to their acid or neutral character, and the acid with which they are combined; in case of necessity they may be converted into the sulphate or hydrochloride.

Resorcinol.

$$C_6H_4 \begin{array}{l} OH(1) \\ OH(3) \end{array} \qquad \text{Molec. wt. } 110.05.$$
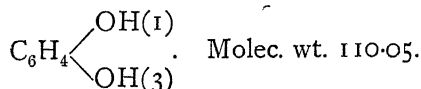
Resorcinol comes into commerce in either a crystallised or sublimed form. It crystallises in colourless plates or prisms possessing a faint, characteristic smell. It melts at $110°\text{-}111°$, and boils at $276°$. It dissolves in 1 part of water, 0.75 parts of alcohol (90 per cent.), readily in ether and glycerol, and sparingly in benzene, chloroform, petroleum spirit, and carbon bisulphide. The aqueous solution of resorcinol reacts acid to litmus paper. On warming 0.1 g. of resorcinol carefully with 0.2 g. of tartaric acid and 20 drops of sulphuric acid, a deep carmine-red solution results. The aqueous solution is coloured violet by ferric chloride, and is precipitated by basic lead acetate, but not by the normal lead acetate.[1]

Tests for Impurities.

Inorganic Matter.—No appreciable residue should remain on heating 1.0 g. of resorcinol.

Free Acids.—Since resorcinol reacts acid, testing with litmus paper as a test for free acids, such as salicylic acid, which was formerly usual, is useless. Larger quantities of acid are, therefore, best detected by titration with $N/1$ alkali. If 1 g. of resorcinol be dissolved in 10 c.c. of alcohol (about 85 per cent. by weight), and a few drops of lacmoid solution added, a red-coloured solution is obtained, which should be turned a violet-blue on the addition of 1 drop of $N/10$ potassium hydroxide solution.

Di-Resorcinol.—This impurity is only found in sublimed resorcinol. 1 g. of resorcinol should dissolve in 20 c.c. of water, giving a perfectly clear solution.

Phenol.—It should not be possible to detect a smell of phenol on warming the above aqueous solution.

Quantitative Estimation.

This is carried out in a similar manner to Koppeschaar's[2] method of estimating phenol. The aqueous solution of resorcinol (1-2 per cent.)

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[1] For colour reactions, cf. *Merck's Reag.-Verz.*, 1908, p. 299.
[2] *Cf.* Vol. II., Part II., p. 823.

is treated with excess of standardised bromine water, or, better, with an acidified solution of potassium bromide and bromate, the excess of bromine being determined by titration with $N/1$ sodium thiosulphate after the addition of potassium-iodide. Tribromoresorcinol is formed in the reaction with bromine, which is difficultly soluble in water.[1]

Saccharin.

$$C_6H_4 \big\langle \begin{array}{c} CO \\ SO_2 \end{array} \big\rangle NH \ (1:2). \quad Molec. \ wt. \ 183\cdot12.$$
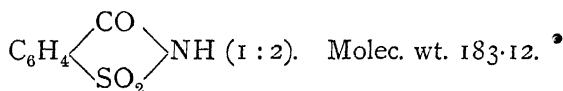
Pure saccharin (ortho-benzoyl sulphone-imide) comes into commerce as a white, odourless, crystalline powder. It is a strong acid which decomposes acetates and forms well-defined salts. Saccharin melts at 224°. It disolves in 400 parts of water, in 30 of alcohol, in 1900 of benzene, and in 120 of ether, and is also readily soluble in ammonia and in the hydroxides and carbonates of the alkalis. It crystallises in small, rhombic leaves from water, in thick prisms from alcohol or acetic acid, in monoclinic crystals from acetone, and in small, hexagonal plates from ether. It sublimes in three-sided plates.

The term "gluside" is adopted in the British Pharmacopœia for saccharin. The sodium salt is known as "crystallose"; it is readily soluble in water, but only sparingly so in alcohol.

On evaporating saccharin down to dryness on the water-bath with nitric acid and then adding, whilst hot, a few drops of water or of 50 per cent. alcohol and a small piece of potassium hydroxide, blue and red streaks of colour are formed on rocking the dish.

Tests for Impurities.

Inorganic Matter.—No appreciable residue should rema... on ignition. Pure saccharin gives but a very small quantity of ash; Langbein found the following percentages of ash in the following brands:—Heyden 0.098 per cent., Fahlberg 0.06 per cent., Bayerl 0.063 per cent., and Monnet 0.04 per cent.[2]

Foreign Organic Matter.—Saccharin should not char on heating, and should not give more than a wine-yellow coloration when dissolved in twenty times its weight of sulphuric acid.

Chlorobenzoic Acid.—0.5 g. of saccharin is moistened with water, mixed with 1 g. of chloride-free calcium carbonate, and the mixture dried and ignited. The ignited residue dissolved in water and nitric acid and made up to 20 c.c. should give no turbidity of silver chloride on adding silver nitrate solution.

[1] *Cf.* C. M. Pence, *J. Ind. Eng. Chem.*, 1911, **3**, 820; *J. Soc. Chem. Ind.*, 1911, **30**, 1369.
[2] *Z. angew. Chem.*, 1896, **9**, 494.

Para-sulphamido Benzoic Acid.—1 g. of saccharin is shaken for a few minutes with 70-80 g. of ether at 15°, the undissolved residue collected on a small filter paper and dried at 100°. The residue should not melt above 224°. The para-acid melts at 280°-283°, and raises the melting point of the above residue, since it is almost insoluble in ether, and becomes concentrated in the residue, practically all the saccharin being dissolved.

Benzoic Acid and Salicylic Acid.—1 g. of saccharin is boiled with 20 c.c. of water, allowed to cool, and filtered. The filtrate should neither be rendered turbid nor coloured violet by ferric chloride.

Mannitol.—0·5 g. of saccharin is dissolved in 10 c.c. of water, and 5 c.c. of sodium carbonate solution (1 : 5) and 10 c.c. of copper sulphate solution (1 : 10) added, the mixture shaken, and filtered after a few minutes; 5 c.c. of sodium hydroxide solution are then added to the filtrate, whether the latter has become turbid subsequent to filtering or not, and the solution heated to boiling. A colourless solution with a brown precipitate should result. A blue solution points to the presence of mannitol.

Quantitative Estimation.

Since the saccharin that comes into commerce contains varying quantities of ortho-benzoyl sulphone-imide, it is best to estimate the latter quantitatively. Commercially saccharin is always judged by sweetness, a method of doubtful value, since the sensitiveness of individuals to the taste of sweetness does or may vary. Since the sweetness depends on the content of sulphone-imide, and is influenced by the content of the para-acid and other constituents which are not sweet but on the other hand of unpleasant taste, a quantitative estimation is really necessary in order to ascertain the purity of the preparation, if the tests given above are insufficient.

The following procedure is given by R. Hefelmann:[1]—10 g. of saccharin are heated in a boiling water-bath for from four to five hours with 100 c.c. of 73 per cent. sulphuric acid, with frequent shaking. Saccharin is thus completely converted into the ammonium salt of sulpho-benzoic acid, whilst the para-acid remains practically unchanged. The decomposition takes place in two stages as follows:—

$$C_6H_4\!\!<^{CO}_{SO_2}\!\!>NH + H_2O = C_6H_4\!\!<^{COOH}_{SO_2.NH_2}$$

$$C_6H_4\!\!<^{COOH}_{SO_2.NH_2} + H_2O = C_6H_4\!\!<^{COOH}_{SO_2ONH_4}$$
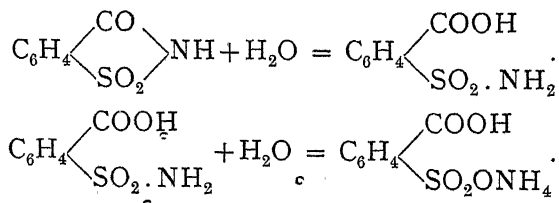
[1] *Pharm. Zentralh.*, **35**, 105 ; *cf.* also Grünhut, *Z. anal. Chem.*, 1897, **36**, 534.

The mixture is then diluted with an equal volume of water, allowed to cool, a small crystal of pure para-acid added, and then allowed to stand for twelve hours. The para-acid thus separates out quantitatively (only after standing for from two to three days if present in very small quantities); it is collected in a Gooch crucible with a double perforated bottom and asbestos filter, washed with small quantities of cold water until the washings show no reaction for sulphuric acid, and then dried at 100° till constant. The weight of the para-acid obtained is somewhat less than it should be, since it is very slightly soluble in water. The error is so small, however, that it may be practically ignored. The para-acid so obtained should melt between 270°-280°.

The filtrate from the para-acid is made up to 500 c.c. in a graduated flask, and 50 c.c. of the solution saturated with ignited magnesia and distilled, the ammonia being collected in $N/2$ sulphuric acid. The quantity of acid neutralised by the ammonia is found by titrating back with $N/2$ potassium hydroxide, and from it the nitrogen content in the saccharin may be calculated. 1 per cent. of nitrogen corresponds to 13·04 per cent. of saccharin. The total nitrogen is determined by boiling 1 g. of saccharin with 25 c.c. of concentrated sulphuric acid and 0·5 g. of mercury in a Kjeldahl flask for two hours, diluting the mixture in a litre flask with 250 c.c. of water, and after adding excess of nitrogen-free sodium or potassium hydroxide solution and about 3 g. of pure zinc dust, the ammonia is distilled off by boiling for one hour and collected in 20 c.c. of $N/2$ sulphuric acid. The content of para-acid may be arrived at from the difference between the two nitrogen determinations.[1]

L. Grünhut[2] has called attention to the fact that many brands of saccharin contain small quantities of ammonium compounds (he found up to 0·046 per cent. of nitrogen as ammonia), and that allowance must be made in such cases by quantitatively estimating the ammonium compounds present.

H. Langbein[3] has shown that the content of the para-acid in saccharin may be readily estimated from the heat of combustion, and states that the results given by this method are very good.

Salicylic Acid.

$$C_6H_4 \begin{cases} OH(1) \\ COOH(2) \end{cases}. \quad \text{Molec. wt. } 138 \cdot 05.$$
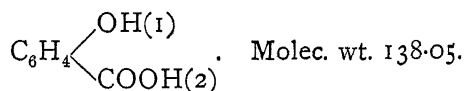
Salicylic acid comes into commerce either as white, odourless needles or as a powder. It melts at 156°-157°, dissolves in about 445 parts of

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[1] Hefelmann, *Pharm. Zeit.*, 41, 379.   [2] *Loc. cit.*
[3] *Z. angew. Chem.*, 1896, 9, 494.

water at 15°, in 15 parts of boiling water, in 2 parts of alcohol or ether, and readily in acetone, chloroform, and carbon bisulphide. It is also soluble in various salt solutions, such as ammonium acetate, ammonium citrate, sodium phosphate, borax, etc., in the hydroxides and carbonates of the alkalis, and in ammonium hydroxide, as well as in glycerol, and in fatty and essential oils.

The aqueous solution of salicylic acid gives a permanent violet coloration with ferric chloride and a green coloration with copper sulphate. Free mineral acids or alkalis prevent or influence these colour reactions.[1]

Tests for Impurities.

Inorganic Matter.—On heating, salicylic acid should volatilise, leaving but a very small quantity of residue; the residue after ignition should not amount to more than 0·1 per cent.

Hydrochloric Acid.—The alcoholic solution (1 : 10) should show no reaction on adding nitric acid and silver nitrate solution.

Foreign Organic Matter.—Salicylic acid should not char on heating. 1 g. of salicylic acid should dissolve to a practically colourless solution in 5 c.c. of sulphuric acid. On dissolving 0·5 g. in absolute alcohol and evaporating off the latter, a perfectly colourless, crystalline mass should remain. The crystals should show no yellow coloration at their points.

Phenol and Salol.—In the absence of salol, 5 g. of salicylic acid should dissolve to a perfectly colourless solution in 100 c.c. of sodium carbonate solution (1 : 5). This solution is shaken up with 30 c.c. of ether, the ether layer syphoned off, again shaken up with 30 c.c. of water, and the ether then allowed to evaporate off on a clock-glass without application of heat. Any residue should not smell of phenol. It is dissolved in a few drops of alcohol and put on one side to evaporate slowly, when salol will crystallise out and may be recognised by its melting point, 42°-43°. In order to detect traces of phenol, 0·25 g. of salicylic acid are rubbed up with 5 c.c. of water, 2 drops of a 2 per cent. alcoholic solution of furfural added, and then 2-3 c.c. of concentrated sulphuric acid slowly run in down the side of the vessel. Minute quantities of phenol cause first a yellow, then a deep blue to violet-blue coloration to be produced at the contact surface of the liquids.[2]

The methods for detecting the following possible impurities in

[1] For identifying reactions, cf. *Merck's Reag.-Verz.*, 1908, p. 300; J. M'Crea, *Analyst*, 1911, **36**, 540; H. C. Sherman and A. Gross, *J. Ind. Eng. Chem.*, 1911, **3**, 492; *J. Soc. Chem. Ind.*, 1911, **30**, 979; E. Barral, *Bull. Soc. Chim.*, 1912, **11**, 417; *J. Soc. Chem. Ind.*, 1912, **31**, 457. For reactions to distinguish salicylic acid from phenol and resorcinol, cf. *Z. anal. Chem.*, 1889, **28**, 712, and *J. Soc. Chem. Ind.*, 1908, **27**, 1131.

[2] Carletti, *Pharm. Zeit.*, 1907, **52**, 1013; 1908, **53**, 192.

salicylic acid are lengthy and complicated; reference is given to the original publications :—

Cresotinic acids, p-hydroxy-benzoic acid, and hydroxy-phthalic acid.[1] *Homologues of salicylic acid*[2] *and impurities in salicylic acid used for physiological purposes.*[3]

Quantitative Estimation.

1 g. of salicylic acid, dried at 50°-60°, is dissolved in 90 per cent. alcohol, and made up to 100 c.c. 10 c.c. of this solution is titrated to a pink colour with $N/10$ potassium hydroxide, using phenolphthalein as indicator. 1 c.c. of $N/10$ potassium hydroxide corresponds to 0·01380 g. of salicylic acid, or 1 g. of salicylic acid requires 72·4 c.c. of $N/10$ potassium hydroxide. If small differences are found in the titrations and the qualitative examination has shown inorganic matter, phenol, and salol to be absent, this points to a content of homologous acid or of cresotinic acid, in which case they should be specially tested for.

According to J. Messinger and G. Vortmann,[4] salicylic acid may also be estimated iodometrically even in presence of benzoic acid. This method has also been studied by J. M. Wilkie.[5]

Salol.

$$C_6H_4 \begin{cases} OH(1) \\ COOC_6H_5(2) \end{cases}$$. Molec. wt. 214·08.
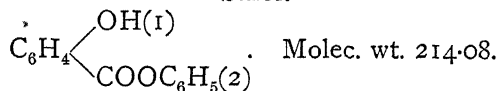
Salol, the phenyl ester of salicylic acid, crystallises in colourless, rhombic plates, possessing a faint aromatic odour. It melts at 42°-43°, dissolves in 10 parts of alcohol and 0·3 parts of ether, but is practically insoluble in water.

The alcoholic solution of salol gives a violet coloration with ferric chloride solution. If 0·5 g. of salol be dissolved in hot sodium hydroxide solution and an excess of hydrochloric acid added, salicylic acid separates out and the solution smells of phenol.

Tests for Impurities.

Free Acid.—On sprinkling powdered salol on blue litmus paper moistened with water, the paper should not be reddened.

Salicylic Acid.—A solution of 0·1 g. of salol in 5 c.c. of ether is poured over some 10 per cent. ferrous sulphate solution in a test tube. If traces of salicylic acid be present, a violet ring is produced in a short time at the contact surface of the two liquids.

Foreign Organic and Inorganic Matter, such as salicylic acid,

[1] *Z. anal. Chem.*, 1890, **29**, 476. [2] *Pharm. Zentralh.*, **29**, 635 [3] *Ibid.*, **32**, 92.

[4] *Ber.*, 1890, **23**, 2755 ; *J. Soc. Chem. Ind.*, 1890, **9**, 1070.

[5] *J. Soc. Chem. Ind.*, 1911, **30**, 398.

sodium phenate, sodium salicylate, sodium chloride, and sodium sulphate or phosphate. Not more than 0·5 mg. of residue should remain on igniting 0·5 g. of salol.

On shaking 2 g. of salol with 100 c.c. of water and filtering, the filtrate should show no reaction with either dilute ferric chloride solution, silver nitrate solution, or barium chloride solution.

Santonine.

$$C_{15}H_{18}O_3. \quad \text{Molec. wt. 246·14.}$$
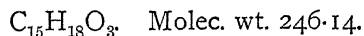
Santonine crystallises in small, colourless, odourless, glistening, rhombic plates, possessing a bitter taste and melting at 170°. It dissolves in about 5000 parts of water at 15°, in 250 parts of boiling water, in 44 parts of alcohol at 15°, in 3 parts of boiling alcohol, in 4 parts of chloroform, in 125 parts of ether, in concentrated acids, in fatty and essential oils, in the hydroxides and carbonates of the alkalis, and is practically insoluble in petroleum spirit.

No coloration should be produced on shaking up 0·1 g. of santonine with a cold mixture of 10 c.c. of sulphuric acid and 10 c.c. of water; on heating this mixture nearly to boiling and then adding several drops of ferric chloride, a violet coloration is produced.[1]

Tests for Impurities.

Inorganic Matter.—Not more than 0·5 mg. of residue should remain on igniting 1 g. of santonine.

Organic Impurities.—Santonine should not be immediately coloured on moistening with either sulphuric acid or with nitric acid.

Free Acids.—A hot solution of 1 g. of santonine in 10 c.c. of alcohol should react neutral.

Citric acid, which is sometimes found in santonine as an adulterant, is tested for as follows:—If by the foregoing test the presence of an acid is indicated, then 0·2 g. of the sample are placed on a watch-glass in a drying oven for a quarter of an hour, at a constant temperature of 115°. If the santonine is adulterated with citric acid a completely molten, yellow-coloured mass will result.[2]

Strychnine.

$$C_{21}H_{22}O_2N_2. \quad \text{Molec. wt. 334·20.}$$
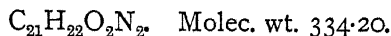
Strychnine comes on to the market as a white, crystalline powder or in colourless, rhombic crystals which melt at 266°. It dissolves in 6600 parts of cold, and in 2500 parts of boiling water, in 160 parts of cold,

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[1] For identifying reactions, cf. *Merck's Reag.-Verz.*, 1908, p. 300.
[2] *Boll. chim. farm.*, 1908, p. 7.

and in 12 parts of boiling 90 per cent. alcohol, in 6 parts of chloroform, and sparingly in ether, benzene, amyl alcohol, and carbon bisulphide; it is practically insoluble in absolute ether and in absolute alcohol. It chars on burning.[1]

The tests are the same as for strychnine nitrate.

Strychnine Nitrate.

$$C_{21}H_{22}O_2N_2 . HNO_3.$$ Molec. wt. 397·21.
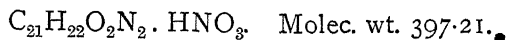
Strychnine nitrate crystallises in colourless and odourless needles possessing a very bitter taste. It dissolves in 90 parts of water, in 70 parts of 90 per cent alcohol, and is practically insoluble in ether, chloroform, and carbon bisulphide.

On adding potassium bichromate solution to an aqueous solution of strychnine nitrate, reddish-yellow crystals separate out, which, when added to sulphuric acid, become transitorily coloured a blue-violet.

Tests for Impurities.

Inorganic Matter.—No residue should remain on igniting 1 g. of strychnine nitrate.

Chloride and Sulphate.—The aqueous solution (1 : 100) should show no reaction with either silver nitrate or with barium chloride solution.

Brucine.—On being rubbed up with nitric acid, strychnine nitrate should be coloured yellow but not red.

Organic Impurities.—Strychnine nitrate should dissolve to a colourless solution in sulphuric acid, and without charring.

Quantitative Estimation.

Strychnine nitrate may be estimated volumetrically under the conditions given for quinine hydrochloride (p. 381). 1 c.c. of $N/5$ potassium hydroxide corresponds to 0·07944 g. of strychnine nitrate.

The free base may be estimated volumetrically in the same way as morphine (p. 365), or also in alcoholic solution, using lacmoid as indicator. 1 c.c. of $N/10$ hydrochloric acid is = 0·03342 g. of strychnine.

Sulphanilic Acid.

$$C_6H_4{<}^{NH_2(1)}_{SO_2OH(4)} +2H_2O.$$ Molec. wt. 209·17.
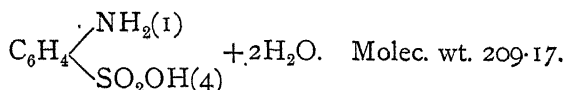
Sulphanilic acid crystallises in colourless, needle-like crystals, possessing no definite melting point, but which char on heating to 280°-

[1] For identifying reactions, cf. *Merck's Reag.-Verz.*, 1908, p. 301.

300°. It is only sparingly soluble in cold water (in about 160 parts), but more readily in hot water; it is insoluble in alcohol, ether, and benzene.

If a few small crystals of sulphanilic acid be dissolved in 50 c.c. of water, and an equal quantity of a-naphthylamine sulphate added, the addition of a drop of an aqueous solution of sodium nitrate produces a cherry-red coloration which quickly changes to yellowish-red with separation of a brownish-red precipitate.

Tests for Impurities.

Inorganic Matter.—No appreciable residue should remain on igniting 1.0 g. of sulphanilic acid.

Sulphuric Acid (Aniline Sulphate).—A solution of 1 g. of sulphanilic acid in 25 c.c. of boiling water should show no change on adding a few drops of barium chloride solution.

Hydrochloric Acid (Aniline Hydrochloride).—On shaking up 1 g. of sulphanilic acid with 20 c.c. of water and filtering, the filtrate should, at most, only give a faint opalescence on adding a few drops of nitric acid and silver nitrate solution.

Quantitative Estimation.

1 g. of sulphanilic acid is dissolved in 10 c.c. of $N/1$ sodium hydroxide and some water, and titrated with $N/1$ hydrochloric acid, using phenolphthalein as indicator. 1 c.c. of the $N/1$ sodium hydroxide used in neutralisation corresponds to 0.2092 g. of sulphanilic acid. The titration of sulphanilic acid with sodium nitrite is more reliable; this, together with other methods of estimation, is described in the section on "Organic Dyes," Vol. II., Part II., pp. 884-5. It is to be borne in mind that sulphanilic acid effloresces readily, and that, in consequence, high results may be obtained.

Sulphonal.

$$CH_3 \diagdown C \diagup SO_2C_2H_5$$
$$CH_3 \diagup \ \ \diagdown SO_2C_2H_5$$

Molec. wt. 228.27.
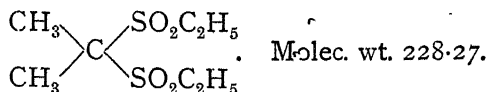
Sulphonal crystallises in colourless, tasteless, and odourless prisms which melt at 125°-126° and boil at about 300° with slight decomposition. It dissolves in 15 parts of boiling water and in 500 parts of water at 15°, in 2 parts of boiling alcohol and in 65 parts at 15°, and in about 135 parts of ether. The solutions of sulphonal react neutral. On heating sulphonal with powdered charcoal, a smell of mercaptan is evolved.

Tests for Impurities.

Inorganic Matter.—Not more than 0·5 mg. of residue should remain on igniting 0·5 g. of sulphonal.

Free Acids.—Powdered sulphonal placed on to blue litmus paper moistened with water should not redden the paper.

Sulphuric Acid and Hydrochloric Acid.—1 g. of sulphonal is dissolved in 50 c.c. of boiling water, the solution allowed to cool and then filtered. Barium chloride solution is added to one-half of the filtrate, and silver nitrate solution to the other half. In neither case should a turbidity or change be produced.

Foreign Organic Matter.—1 g. of sulphonal should not become coloured on pouring 10 c.c. of sulphuric acid over it.

Mercaptol $((CH_3)_2C(SC_2H_5)_2)$ *and Oxidisable Matter.*—No garlic-like odour should be produced on boiling 1 g. of sulphonal with 50 c.c. of water. After cooling and filtering this solution, 10 c.c. are taken and one drop of potassium permanganate solution (1 : 1000) added. The colour of the permanganate should not be immediately discharged.

Note.—To detect sulphonal in trional and tetronal, use is made of the differences in their solubility in ether; 10 c.c. of ether at 15° dissolve about 0·07 g. of sulphonal, 0·5 g. of trional, and 1 g. of tetronal.[1] The undissolved residue is detected as sulphonal by its reactions and melting point.

Tannin (Tannic Acid).

$$C_{14}H_{10}O_9 + H_2O. \quad \text{Molec. wt. } 358 \cdot 11.$$
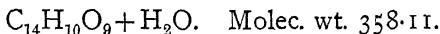
Tannin comes into commerce as a yellow amorphous powder, or as "crystalline tannin" or "needle tannin." It should possess only a faint smell and should dissolve to form perfectly clear solutions in water and in alcohol (about 85 per cent. by weight). It is soluble in 1 part of water, 2 parts of alcohol, 8 parts of glycerol, and in ethyl acetate; it dissolves sparingly in ether (according to its content of alcohol), and is practically insoluble in chloroform, petroleum spirit, benzene, and carbon bisulphide. Alcoholic and aqueous solutions of tannin are dextrorotatory.

The aqueous solution of tannic acid gives a blue-black precipitate with ferric chloride, the precipitate dissolving on addition of sulphuric acid. Dilute solutions only give a blue-black coloration. Tannin precipitates solutions of tartar emetic, alkaloids, albumin, and glue.[2] Reactions distinguishing gallic from tannic acid are described under gallic acid (p. 353).

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[1] E. Gabutti, *J. Pharm. Chim.*, 1907, **25**, 183 ; *J. Soc. Chem. Ind.*, 1907, **26**, 636.

[2] For identifying reactions of tannin, cf. *Merck's Reag.-Verz.*, 1908, p. 294.

Tests for Impurities.

Inorganic Matter (Zinc).—Not more than 5 mg. of residue should remain on igniting 4 g. of tannin. The residue, when dissolved in 2 c.c. of acetic acid and diluted with 8 c.c. of water, should give not more than a faint opalescent turbidity on adding sulphuretted hydrogen water.

Sugar and Dextrin.—On mixing 10 c.c. of a tannin solution (1 : 5) with 10 c.c. of alcohol (about 85 per cent. by weight) the solution should remain clear for half an hour; no turbidity should be produced on the further addition of 5 c.c. of ether.

Gallic Acid.—Even the purest tannin contains traces of gallic acid, which may be recognised by the red coloration produced on treating a solution of tannin with potassium cyanide solution. Larger quantities of gallic acid may be estimated by the method given under gallic acid (p. 354).

Water.—On drying 1 g. of tannin at 100° till constant, the loss of weight should not exceed 12 per cent.

Quantitative Estimation.

The quantitative estimation of tannin may be carried out by the methods described in the section on "Vegetable Tanning Materials," this Vol., pp. 452 *et seq.*

Theobromine.

$$C_5H_2(CH_3)_2O_2N_4. \quad \text{Molec. wt. } 180.10.$$
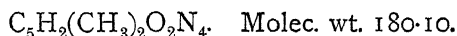
Theobromine is a white, crystalline powder without smell, and possessing a bitter taste. At about 290° most of it sublimes undecomposed, without previously melting. It dissolves in about 1600 parts of cold, and in 150 parts of boiling water, in about 4000 parts of cold, and 400 parts of boiling absolute alcohol, and in 100 parts of boiling chloroform. The aqueous solution reacts neutral. Theobromine dissolves both in acids and in dilute alkalis.

On evaporating a solution of theobromine on the water-bath with chlorine water, a reddish-yellow residue is obtained which becomes coloured purple-red on adding a drop of ammonia. C. Gérard[1] gives the following reaction for distinguishing theobromine from caffeine :—
1 c.c. of a 10 per cent. silver nitrate solution is added to a mixture of 0·05 g. of theobromine, 3 c.c. of water, and 6 c.c. of sodium hydroxide solution, and after heating to 60° the resulting clear solution is allowed to cool; when cold, the mixture solidifies to a transparent jelly. Caffeine does not give this reaction.

[1] *J. Pharm. Chim.*, 1906, **23**, 476; *J. Chem. Soc. Abstr.*, 1906, **90**, 507.

Tests for Impurities.

Theobromine should dissolve to form colourless solutions in sulphuric acid, in nitric acid, and in ammonia. The cold, saturated, aqueous solution should not be precipitated by iodine solution.

Caffeine.—If 0·1 g. of theobromine be repeatedly shaken during one hour with 10 c.c. of chloroform and then filtered, 3 c.c. of the filtrate should not leave more than 0·001 g. of residue when evaporated on the water-bath.

Water and Inorganic Impurities.—1 g. of theobromine should not lose appreciably in weight on drying at 100°, and should volatilise on heating without leaving an appreciable residue (0·5 mg.).

In medicine, in place of pure theobromine, the double salts theobromine-sodium acetate, theobromine-sodium benzoate, and theobromine-sodium salicylate are mostly used. These preparations, of which the last-named is the most important, are very soluble in water, but the solutions are rendered turbid by the action of the carbon dioxide in the air, since acids cause a separation of free theobromine.

Theobromine-Sodium Salicylate.

This is a double salt of theobromine and sodium salicylate with sodium hydroxide, having the composition :—

$$C_7H_7NaO_2N_4 . H_2O . C_6H_4(OH)(COONa)$$
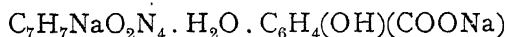
and containing approximately 45 per cent. of theobromine. It forms a white, odourless powder, possessing a sweet, and at the same time somewhat alkaline taste, and dissolves in its own weight of water. The aqueous solution is alkaline to litmus paper, and gives a violet coloration with ferric chloride solution. Hydrochloric acid precipitates salicylic acid from the aqueous solution, and also after some time theobromine, as a white precipitate which is completely redissolved by sodium hydroxide, but not by ammonia.

Tests for Impurities.

Sodium Carbonate and Decomposition Products.—Theobromine-sodium salicylate should dissolve in sulphuric acid without effervescence, and to a colourless solution.

Caffeine.—On shaking up a solution of 1 g. of theobromine-sodium salicylate in 10 c.c. of sodium hydroxide solution with 10 c.c. of chloroform, not more than 0·005 g. of residue should remain on evaporation of the chloroform extract.

Water.—The preparation should not lose more than 10 per cent. in weight on drying for one hour at 100°.

Quantitative Estimation.

Free Sodium Hydroxide.—If 1 g. of the anhydrous salt or a correspondingly larger quantity of the hydrated salt be dissolved in 100 c.c. of previously boiled water, the solution, after the addition of a few drops of phenolphthalein, should not require more than 2·9 c.c. of $N/1$ acid for neutralisation.

Combined Sodium Hydroxide.—1 g. of the salt, dissolved in 400 c.c. of water, should not require more than 2·9 c.c. of $N/1$ acid for neutralisation, using methyl orange as indicator.

Sodium Salicylate.—1 g. of the anhydrous salt is dissolved in water, acidified with 3 c.c. of dilute sulphuric acid, and the salicylic acid completely extracted with ether. The residue obtained on evaporation of the ethereal extract, when dissolved in alcohol and some water, should require 26·5 to 27·5 c.c. of $N/10$ sodium hydroxide for neutralisation, using phenolphthalein as indicator. This volume of $N/10$ sodium hydroxide corresponds to 42-44 per cent. of sodium salicylate.[1]

Theobromine.—The following method, due to E. Anneler,[2] yields results which are accurate to within 0·1 per cent. :—1 g. of theobromine-sodium salicylate is dissolved in about 10 c.c. of water in a small separating funnel, the theobromine and salicylic acid precipitated by adding 3 c.c. of hydrochloric acid (10 per cent.), and after adding a drop of phenolphthalein solution and concentrated barium hydroxide solution (till red), the solution is extracted three times successively with a 20 per cent. solution of phenol in chloroform. The chloroform and phenol are then evaporated off on the water-bath, when a residue of pure theobromine is left, which is weighed.

The method described by O. Frey,[3] in which the theobromine is precipitated from an acid solution by means of ammonia, yields only comparative results, as the separation of the theobromine is incomplete.

Thymol.

$$C_6H_3 \overset{\diagup CH_3(1)}{\underset{\diagdown C_3H_7(4)}{-OH(3)}}. \quad \text{Molec. wt. } 150 \cdot 11.$$
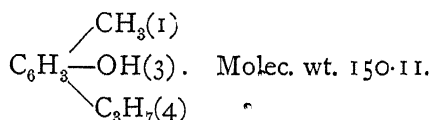
Thymol forms colourless, hexagonal crystals which have a thyme-like smell and an aromatic taste. It melts at 50°-51°, and boils at 228°-230°. It sinks in water, since in the solid state it has a sp. gr. of 1·028, but is lighter than water when melted. Thymol dissolves readily in alcohol, ether, chloroform, carbon bisulphide, and petroleum spirit, as well as in sodium hydroxide solution; it is only sparingly

[1] *Cf.* O. Frey, *Z. d. Oesterr. Apoth.-Ver.*, 1909, **47**, 433 ; *J. Soc. Chem. Ind.*, 1909, **28**, 1166.
[2] *Pharm. Zeit.*, 1910, **55**, 205.   [3] *Loc. cit.*

soluble in water (1 : 1100). On dissolving a small crystal of thymol in •hot potassium hydroxide solution and adding a few drops of chloroform, the mixture assumes a violet coloration on shaking. If 1 g. of thymol be dissolved in 4 g. of sulphuric acid, and this solution after being gently warmed for five minutes be poured into 50 c.c. of water, and then lead carbonate added in excess and the mixture allowed to stand for half an hour at about 40° with frequent shaking, on filtering, the filtrate gives a violet coloration on the addition of ferric chloride. Thymol turns a rose-red colour on heating with sulphuric acid to about 60°, and is converted into thymol sulphonic acid. A bluish-green coloration is produced by dissolving a small crystal of thymol in 1 c.c. of glacial acetic acid and then adding 6 drops of sulphuric acid and 1 drop of nitric acid.[1]

Tests for Impurities.

Inorganic Matter.—No appreciable residue should remain on igniting 1 g. of thymol.

Free Acids.—Neither an aqueous nor alcoholic solution of thymol should redden blue litmus paper.

Phenol.—On adding bromine water to the aqueous solution (1 : 1000), only a milky turbidity should be produced, and no crystalline precipitate. The same solution should not give a violet coloration with ferric chloride.

Quantitative Estimation.

J. Messinger and G. Vortmann[2] give the following method, which is both rapid and convenient :—2·5 g. of thymol are dissolved in 25 c.c. of sodium hydroxide solution (sp. gr. 1·17), and the solution made up with water to 250 c.c. 25 c.c. of this solution are transferred to a 250 c.c. measuring flask, and 100 c.c. of $N/10$ iodine solution added, whereby a brownish-red precipitate is produced. After acidifying with dilute sulphuric acid the flask is filled up to the mark, the contents filtered, and the excess of iodine titrated with $N/10$ sodium thiosulphate. From the number of cubic centimetres of iodine solution used, the quantity of iodine used for 1 g. of thymol is calculated, and this figure, multiplied by 29·561, gives the percentage content of thymol.

Vanillin.

$$C_6H_3{<}^{COH(1)}_{OH(4)}{-}OCH_3(3).$$ Molec. wt. 152·06.
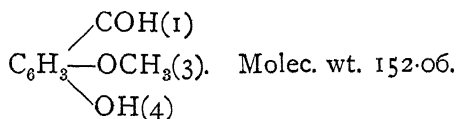
Artificially prepared vanillin is similar in all its properties to that

[1] For other identifying reactions, cf. *Merck'* *Reag.-Verz.*, 1908, p. 301.

[2] *Ber.*, 1890, **23**, 2753 ; *J. Soc. Chem. Ind.*, 1890, **9**, 1070 ; *J. prakt. Chem.*, 1900, **61**, 237 ; *J. Soc. Chem. Ind.*, 1900, **19**, 568.

obtained from the vanilla bean. It comes into commerce as colourless or slightly yellow needles which possess a vanilla-like smell. It melts, when quite pure, at 83,° and boils at 285°. Vanillin dissolves in 100 parts of water at 15° and in 20 parts of boiling water, and readily in alcohol, ether, chloroform, and carbon bisulphide. The cold, saturated, aqueous solution gives a violet coloration with ferric chloride. A brownish coloration is produced on warming this mixture, and fine needles (dehydrodivanillin) separate out. A deep red coloration is produced on adding 10-15 c.c. of concentrated hydrochloric acid (sp. gr. 1.19) to a solution of 0.1 g. of vanillin and 0.2 g. of pyrogallol in 5 c.c. of alcohol.[1]

Tests for Impurities.

Inorganic Matter.—Not more than 0.5 mg. of residue should remain on igniting 1 g. of vanillin.

Foreign Organic Matter (Sugar, Tarry Substances).—0.1 g. of vanillin should dissolve in 20 c.c. of sulphuric acid to a pale yellow solution; no browning or charring should take place.

Coumarin may be readily detected in vanillin by fusing with potassium hydroxide, salicylic acid and acetic acid being produced, which may be easily identified; vanillin yields protocatechuic acid.

W. Hess and A. Prescott[2] detect coumarin by passing dry ammonia gas through an ethereal solution of vanillin, whereby the aldehyde-ammonia compound of vanillin is separated. On shaking with ammonium hydroxide, all the vanillin is extracted from the ethereal solution, whilst coumarin remains dissolved in the ether and may be recognised in the dried residue remaining after evaporating off the ether, by its melting point (67°).

Acetanilide and Benzoic Acid, which may be present in commercial vanillin as adulterants, may be detected by their identifying reactions.

Quantitative Estimation.

1 g. of vanillin is dissolved in 25 c.c. of alcohol and 25 c.c. of alcoholic $N/2$ potassium hydroxide, and the excess of alkali titrated back with $N/2$ hydrochloric acid, using phenolphthalein as indicator. The number of cubic centimetres of potassium hydroxide used, multiplied by 0.07603, gives the content of vanillin.

The colorimetric method due to F. Moerk[3] only gives approximate values; it is based on the bluish-green coloration produced

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[1] For other colour reactions, cf. *Merck's Reag.-Verz.*, 1908, p. 302.

[2] *Pharm. Rev.*, 1899, **17**, 7; *J. Soc. Chem. Ind.*, 1899, **18**, 397; *J. Amer. Chem. Soc.*, 1899, **21**, 256; *J. Soc. Chem. Ind.*, 1899, **18**, 525.

[3] *Z. anal. Chem.*, 1893, **32**, 242; *J. Soc. Chem. Ind.*, 1892, **11**, 637.

by ferrous sulphate in a solution of vanillin to which bromine has been added.[1]

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[1] *Cf.* W. S. Hubbard, *J. Ind. Eng. Chem.,* 1912, 4, 669 ; *J. Soc. Chem. Ind.,* 1912, 31, 949, and O. Folin and W. Denis, *J. Ind. Eng. Chem.,* 1912, 4, 670 ; *J. Soc. Chem. Ind.,* 1912, 31, 949.

INDIA-RUBBER AND RUBBER GOODS.

By F. FRANK, Ph.D., and E. MARCKWALD, Ph.D., Berlin. English translation
revised by W. A. CASPARI, Ph.D., B.Sc.

A.—CRUDE AND VULCANISED RUBBER.

INDIA-RUBBER, or rubber for short, is the name given to the solid matter which exists in aqueous suspension in the latex of various plants, from which it is separated by chemical or mechanical methods. Rubber-yielding plants belong chiefly to the botanical families of *Euphorbiaceæ*, *Asclepiadeæ*, and *Apocynaceæ*; their habitat is South and Central America, Africa, the Malay Peninsula, and the islands of the Malay Archipelago. Whereas the bulk of crude rubber still comes from wild trees, a very large quantity is now produced from plantations. A great variety of crude rubbers is known to commerce, differing not only in origin and external appearances, but also in physical and chemical characteristics. The substance which is common to all of them, and which makes rubber what it is, is the caoutchouc hydrocarbon. This substance was named polyprene by C. O. Weber, and the name, though based on assumptions which were subsequently refuted, is still in use. Its chemical constitution has been shown by C. Harries[1] to be that of a dimethyl-*cyclo*-octadiene, on evidence derived not only from the degradation of rubber, but also from its synthesis from isoprene, first observed at a much earlier date by Tilden.[2] Isoprene has been prepared synthetically by Euler,[3] and its constitution is well known. The empirical formula of the rubber hydrocarbon is $(C_{10}H_{16})_n$. The physical differences in rubbers of various origin may in all probability be accounted for by variations in molecular structure, and in the degree of polymerisation. Apart from this, crude rubbers also differ widely in the amount and nature of the foreign matter associated with them, which may either have been derived from the latex, or may have been added in the preparation, either through ignorance or by

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[1] *Ber.*, 1905, 38, 1195.   [2] *Chem. News*, 1882, 46, 120.

[3] *Ber.*, 1898, 30, 1989.

way of adulteration. Again, ingredients not of the nature of rubber may have been produced by decomposition of the rubber itself whilst lying by, or during shipment. Whenever, then, the word "rubber" is used in the sequel, it will be understood that this term covers a series of substances which are closely related chemically, but need by no means be identical.

THE EXAMINATION OF CRUDE RUBBER.

The identification and valuation of crude rubbers, the market prices of which cover a wide range, is carried out by practical experts with the aid of such external properties as colour, odour, taste, springiness, shape, and so forth.[1] These criteria, valuable as they are, do not rank as analytical methods, and are accordingly outside the scope of this Section.

Crude rubbers always contain certain associated substances in proportions which vary not only for the different sorts but also for different samples of the same sort. These are, first and foremost, moisture, together with organic and inorganic impurities, such as bark, leaves, sand, pebbles, clay, soluble matter, proteids, etc. The cleansing process, which is the first stage in rubber manufacture, eliminates the greater part of these impurities, which are summed up under the heading of "washing loss." To determine washing loss on a few grams of rubber taken from bulk by the laboratory methods of desiccation, incineration, etc., would be of no value, because the impurities are very irregularly distributed, so that the accurate drawing of a minute sample is not feasible. The small-scale determination of washing loss must be made on a carefully drawn sample of at least 100-250 g., and must be conducted similarly to the method adopted on the manufacturing scale; that is, by means of washing rollers. A laboratory washing mill should follow, except as regards dimensions, the construction of a full-scale mill.

Rubber thus cleansed is an amorphous, springy substance of sp. gr. 0·92-0·96, of a colour ranging from light yellow to dark brown, almost black. Its most salient property is its elasticity, which is not much affected by changes of temperature between $+4°$ and $+50°$. At low temperatures rubber becomes hard, at high temperatures soft and sticky, and on returning to normal temperature it regains its elasticity very slowly, or even fails to regain it completely. Freshly cut surfaces of rubber, when gently pressed together, have the property of adhering with a firmness equal to the cohesion of the material itself.

[1] See Henriques-Soskin, *Gummi-Kalender*, 1908 ; Marckwald and Frank, *Herkommen und Chemie des Kautschuks*, 1904 ; and other technical literature.

Washed rubber contains, beside the rubber hydrocarbon, varying amounts of organic oxygenated substances known generically as "rubber resins," the chemical nature of which is not as yet cleared up. According to the currently received view, a crude rubber is the more valuable the less resin it contains; it would be more correct to say that quality depends not only on the amount, but even more on the nature of the resins present. Rubber resins have the property, by which they are distinguished from rubber proper, of being soluble in alcohols, acetone, ethyl acetate, etc.

I. DÉTERMINATION OF RESIN, MOISTURE, AND ASH.

5 g. of washed and dried rubber are extracted with boiling acetone in a Zuntz extractor, or other apparatus working on the same principle, for five to eight hours. A modified form of Zuntz extractor, devised by W. A. Caspari, which has the advantage that there are no cork connections, is shown in Fig. 51; the water - cooled condenser (shown at the side) slides into, and rests loosely on, the mouth of the extractor.
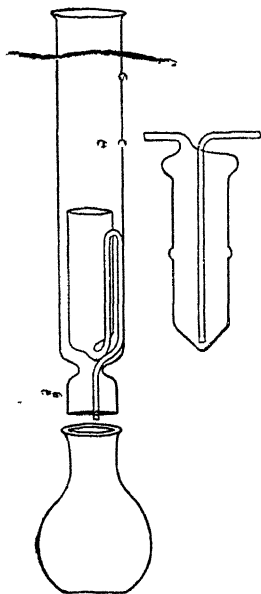
To facilitate extraction, the sample should be rolled into thin sheets, or cut into the narrowest possible strips and spread on a strip of muslin; a second piece of muslin is superposed, and the whole is rolled around a glass rod (Fig. 52). The extract is distilled on a water-bath and the flask containing the residue dried at 95°-100° till constant. The increase in weight of the flask represents resin,

FIG. 51.
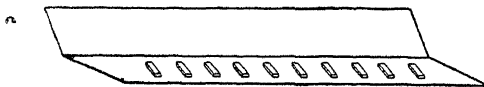
FIG. 52.

generally so-called; but a better term would be "acetone extract," since it may also contain a little depolymerised rubber. The residual material is freed from acetone by drying at 75°-80°, or at a lower temperature *in vacuo*. The total loss thus sustained by the rubber, minus the resin-content found, is taken as approximately representing the moisture-content. Rubber of good quality does not, after drying, adhere to the fabric.

The following Table shows the proportion of resin in some of the

more important sorts of crude rubber, referred to washed and dried material :—

Para (1·0-4·5)	.	.	.	average	2·0	per cent.
Bolivian	.	.	.	,,	3·1	,,
Rio Sheet	.	.	.	,,	8·3	,,
Colombian	.	.	.	,,	5·0	,,
Upper Congo (4·0-9·0)	.	.	.	,,	6·5	,,
Lower Congo	.	.	.	,,	4·5	,,
Lagos	.	.	.	,,	4·5	,,
Sierra Leone (4·0-7·0)	.	.	.	,,	5·5	,,
Red Kassai	.	.	.	,,	4·4	,,
Java	.	.	.	,,	4·0	,,
Borneo	.	.	.	,,	10·5	,,
Ceylon Plantation, *Hevea*	.	.	,,	3·2	,,	
Plantation, *Kickxia*	.	.	.	,,	7·5	,,
Guayule	.	.	.	,,	18·0	,,
Pontianak	.	.	.	,,	85·0	,,

In rubber manufacture the raw material is usually worked up without any attempt at de-resinification. The determination of the resin-content serves, therefore, mainly to indicate the proportion of hydrocarbon in a crude rubber, and thus to give some idea of its relative value.

An attempt to apply the properties of rubber resins to the identification of the original rubber has been made by F. W. Hinrichsen and J. Marcusson,[1] who determined the optical rotation and the saponification values of various resins. It appears that the resins of Para and Ceylon-Para (*Hevea*) rubbers are optically inactive, whereas those of other rubbers have specific rotations ranging from $+10°$ to $+50°$. The unsaponifiable portion of the resins is that which is responsible for the rotation. As means to the positive identification of rubber sorts, however, these properties, which are affected to some extent by the treatment of the latex and other factors, cannot safely, so far as at present studied, be relied upon.

Beside the determination of resin, it is desirable to carry out a direct determination of moisture. For this purpose the rubber is dried in an ordinary drying oven at $90°-95°$, or *in vacuo* at a lower temperature. The determination of ash and a qualitative examination of the same are also of some value. For the method of incineration, see p. 419.

II. THE DIRECT DETERMINATION OF RUBBER.

Two methods for the direct determination of the rubber hydrocarbon by means of derivatives have been proposed in recent years.

[1] *Z. angew. Chem.,* 1910, 23, 49.

The one is based on the formation of a tetrabromide of dimethyl-*cyclo*-octadiene, which is scarcely if at all soluble in the usual rubber solvents. The other depends upon the formation of a "nitrosite" (Harries) or "nitrosate" (Alexander) which results from the action of nitrous fumes upon rubber. The former derivative, when precipitated, is apt to enclose any insoluble impurities which may be present; nevertheless Budde's form of the tetrabromide method is simple in execution and is capable of giving good results. The nitrous derivatives have the advantage that they can be isolated by means of their selective solubilities; it matters little whether the procedure of Harries or that of Alexander be followed, since very accurate results cannot be obtained in either case without careful previous purification of the crude rubber; either method is sufficiently accurate, however, for an approximate direct determination of the rubber-content.

a. The Tetrabromide Method. (T. Budde.[1])

The dry rubber is cut into small pieces, of which 0.15-0.2 g. is soaked in 50 c.c. of carbon tetrachloride during twenty-four hours. To the solution are added 50 c.c. of brominating reagent, which is made up of 1000 c.c. of carbon tetrachloride, 6 c.c. of bromine, and 1 g. of iodine. The mixture is allowed to stand, with occasional shaking, for six hours. Half the bulk of alcohol is then added and well stirred or shaken in. After standing overnight, the clear supernatant liquid is decanted through an ash-free filter, the precipitate washed with a mixture of two parts of tetrachloride to one of alcohol, and finally kneaded with alcohol alone. The precipitate is then treated during three to four hours with 30-40 c.c. of carbon bisulphide, and again thrown down by the addition of 50 c.c. of petroleum spirit. The liquid is then again filtered through the original filter and the precipitate washed with alcohol. The filter with its solid contents is added to that portion of the precipitate which has remained in the flask, 40 c.c. of $N/5$ silver nitrate solution and 20 c.c. of nitric acid (sp. gr. 1.40) added, and the whole boiled briskly, a funnel being placed in the mouth of the flask.

When all of the rubber bromide has been visibly converted into yellow silver bromide, the liquid is cooled and the excess of nitrate is titrated with $N/5$ ammonium thiocyanate and iron alum by Volhard's method. The amount of silver nitrate used up being thus known, and thence the amount of bromine in the rubber tetrabromide, the rubber itself is calculated by the equation:—

$$\text{Bromine} \times 0.425 = \text{rubber.}$$

[1] *Gummi-Zeit.*, 1909, **24**, 4; *J. Soc. Chem. Ind.*, 1909, **28**, 1140.

b. Nitrosite Methods.

These methods are based on the fact that nitrous gases convert rubber into peculiar yellow derivatives having properties differing radically from those of rubber itself; these were first described by C. Harries.[1] The nitrosite of rubber was first applied to analytical purposes by G. Fendler [2] and by R. Dietrich.[3] Definite analytical procedures were eventually worked out independently by Harries and by Alexander. Although the nitrosites formed in the two methods are not identical, they both give results which suffice for technical purposes. The advantage which rubber nitrosite has over rubber bromide, in that it can readily be purified by solution and reprecipitation, is counter-

FIG. 58.
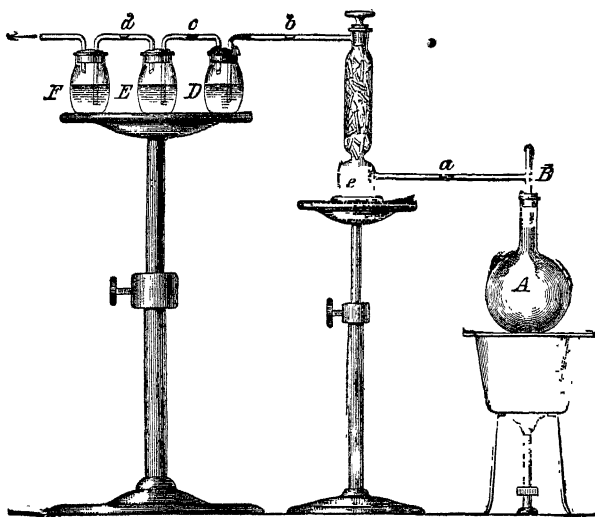
balanced by the fact that the nitrosite is not easy to dry, and is far more troublesome to prepare.

I. *P. Alexander's Method.*[4]—For the evolution of nitrous gases a 500 c.c. flask is half filled with concentrated nitric acid (sp. gr. 1·40), with the addition of four or five granular pieces of starch the size of a pea, and gently warmed on the water-bath. As the evolution of gas slackens, two or three more pieces of starch are added. The apparatus is shown in Fig. 53. A is the flask, B a T-piece for the introduction of starch, and C a drying-tower charged with vitreous phosphoric acid. D, E, and F are the reaction vessels; they are fitted with ground-in

[1] *Ber.*, 1901, **34**, 2991 ; 1903, **36**, 1937.   [2] *Gummi-Zeit.*, 1904, **18**, 848.
[3] *Pharm. Zeit.*, 1903, No. 78.   [4] *Z. angew. Chem.*, 1907, **20**, 1355.

stoppers, into which the tubulures are sealed (see Fig. 54). The joints a, b, c, and d should be ground-in.

Each of the flasks D, E, and F contains a known weight, about 0.5 g., of acetone-extracted rubber, together with 50 c.c. of carbon tetrachloride. Nitrous gases are passed through until the last of the flasks is saturated; they are then disconnected and allowed to stand overnight. The supernatant liquid is now poured off, and the residue dissolved in acetone and filtered, the filter being washed with acetone. The solution is introduced in small quantities at a time, into a weighed flask similar to the reaction vessels, and evaporated in a current of hydrogen at a temperature not exceeding 45°. The solid residue is finally heated in the same way until the weight is constant. The nitrosite is thus obtained in the form of a brown vitreous mass. Frank and Marckwald, in conjunction with L. Weber, have found that in this form the nitrosite retains acetone most tenaciously, so that drying to constant weight is a very tedious operation. They therefore, after distilling off most of the acetone, add ether, and thus precipitate the nitrosite as a powder which admits of easier drying. The ether, moreover, helps to carry off the acetone, and it is sometimes worth while to add repeated portions of ether to the apparently dry powder in order to effect the removal of the last traces of acetone.
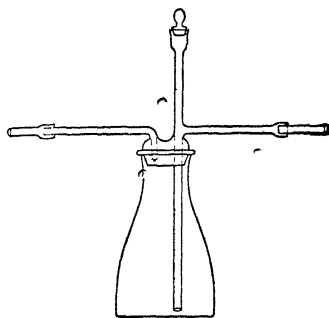
The results are calculated according to the relation :—

1 g. rubber = 2·107 g. Alexander's nitrosate.

II. *C. Harries' Method.*[1]—The apparatus for evolving nitrous gases is the same as above, but they are prepared by heating arsenic trioxide with nitric acid of sp. gr. 1·3. In the modification of Harries' original method recently worked out by Korneck,[2] the determination is carried out as follows :—A weighed quantity of rubber of 0·5-1·0 g., which has been purified by acetone-extraction, or by solution and re-precipitation, is dissolved in 75 c.c. of benzene in a 200 c.c. beaker. Nitrous gases are passed in for an hour or two until the benzene has become dark green, the clotted precipitate being broken up from time to time. After standing for a short time, the solvent is decanted off through a Gooch crucible, and the precipitate is washed, covered with 75 c.c. of fresh benzene, again treated with the gases, and allowed to stand for twenty-four hours. The precipitate is then removed as far as possible from the

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[1] *Ber.*, 1902, **35**, 4429.

[2] *Gummi-Zeit.*, 1910, **25**, 4, 42, 77 ; see also Gottlob, *Z. angew. Chem.*, 1907, **20**, 2213.

beaker and transferred to the crucible; the nitrosite in both vessels is washed with petroleum spirit, and then with absolute ether. The beaker and crucible are dried *in vacuo* for half an hour, and then to constant weight in a drying oven at 80°. The contents of the beaker are finally dissolved in 50 c.c. of warm acetone, which is poured on to the crucible, and both are washed with acetone until free from nitrosite, and are dried to constant weight. The combined net weight of nitrosite thus found is calculated to rubber according to the relation :—

$$\text{1 g. rubber} = 2\cdot125 \text{ g. Harries' nitrosite.}$$

c. Schneider's Method.[1]

Frank and Marckwald adopt the following procedure, which involves some slight modifications of the original method. From 2-4 g. of rubber are weighed out, allowed to swell in 30 c.c. of chloroform, and stirred up with a further quantity of 270 c.c. of chloroform. Dissolution is effected by warming the mixture on the water-bath. Mechanical impurities and certain rubber-like substances containing nitrogen and oxygen remain undissolved; the latter swell up greatly in the solvent and are not always easily recognised as being insoluble. The solution is filtered through fine silk gauze, and the residue is well washed, dried, and weighed.[2] The filtrate, or an aliquot part, is warmed to 60° under a reflux condenser, and alcohol is added, drop by drop, with constant shaking. At first the precipitated matter redissolves; as soon as there is a slight permanent cloudiness, no more alcohol is added. On standing, a considerable quantity of matter is precipitated in the form of flakes; this is collected on silk gauze, washed with alcohol, detached, dried in hydrogen, and weighed. Schneider applies the term α-caoutchouc to this fraction, which is held to be the most valuable constituent of the rubber. To the filtrate 500 c.c. of alcohol are added, which precipitates the second fraction, β-caoutchouc; it is collected and weighed as before. The liquid now remaining is evaporated to dryness, and the residue is repeatedly boiled out with absolute alcohol. By this means the resin is brought into solution, and can · be determined, whilst a final fraction, γ-caoutchouc, remains undissolved.

The first precipitate, α-caoutchouc, is by far the toughest and best portion of the rubber; β-caoutchouc is rather weaker, and γ-caoutchouc is quite soft and sticky. Hence from the amount of γ-caoutchouc present, or, better, from the ratio of the three fractions, some idea of the technical value of the rubber can be gained. It is

[1] *Gummi-Zeit.*, 1902, 16, 874.
[2] *Cf.* D. Spence, *Rep. Inst. Commercial Research in the Tropics*, Liverpool University, No. 13.

not known with certainty whether the insoluble nitrogenous substance referred to above, which is counted as non-rubber, is really devoid of value; it is frequently found to possess a high degree of toughness, so that it ought probably not to be regarded as a detrimental constituent unless present in abnormal amount.

d. G. Fendler's Method.[1]

The following procedure, which is somewhat similar to that of Schneider, has been proposed by Fendler for the valuation of crude rubber. About 3 g. of dry rubber are dissolved in 97 g. of benzene by dint of swelling and shaking, and filtered through glass-wool, the residue being well washed with benzene. This residue consists of the insoluble nitrogenous matter mentioned above and a part of the mechanical impurities, whilst the filtrate holds in solution rubber and resin. An aliquot portion of the filtrate is poured into one and a half times its weight of absolute alcohol, which is kept in agitation during the addition. The rubber hydrocarbon is thus completely precipitated, and is then collected upon glass-wool, dried, and weighed. An error to which the method is subject lies in the tendency of the rubber to carry down resin with it, for which reason it is desirable to warm the solution and the alcohol to 50° or 60° before mixing. The method yields good comparable results in experienced hands if all proper precautions are observed.

e. D. Spence's Method.

After the crude rubber has been washed, a 10 g. sample of the air-dried sheet is dehydrated to constant weight in a vacuum-exsiccator over sulphuric acid. The loss in weight is added to total loss in washing. From 4-6 g. of the dry sample are taken for acetone-extraction in a Soxhlet or Zuntz tube, and the resin is weighed.

The extracted rubber is again dried to constancy in a vacuum-exsiccator and the amount of rubber hydrocarbon contained determined as follows:—A weighed quantity of about 1·5 g. is introduced into a 200 c.c. flask with about 100 c.c. of benzene, and is brought into solution by frequent shaking. A homogeneous solution is generally obtained in a few hours, but it sometimes happens that days are required to effect this; heat should on no account be applied, as no advantage is gained thereby. The solution is eventually made up to 200 c.c. with benzene. An aliquot portion, say 100 c.c., is filtered through a dried and weighed funnel fitted with a wad of glass-wool, which can usually be done in about ten minutes. The filtrate thus obtained, of which the volume

[1] *Gummi-Zeit.*, 1904, **19**, 41.

must be accurately known, is evaporated in a weighed beaker, dried by passing a rapid current of carbon dioxide through the hot beaker, and weighed. This gives the amount of rubber hydrocarbon present, which may be calculated as a percentage either of original or of washed crude rubber.

In order to determine the insoluble impurities, the remainder of the solution in the 200 c.c. flask is copiously diluted with benzene, and filtered through the glass-wool filter previously used. The water retained by the filter is washed with benzene and finally with alcohol, dried, and weighed.

III. THE DETERMINATION OF PROTEIN IN CRUDE RUBBER.

The protein-content of a rubber is frequently of considerable importance in relation to its value. So far as mechanical strength is concerned, the presence of proteid matter is not necessarily a disadvantage; in some kinds of rubber, *e.g.* that from *Kickxia*, the "nerve" appears to increase with the amount of protein present. On the other hand, proteid impurities have a decided effect on the keeping qualities of crude rubber; when there is much protein and much moisture, the putrefaction which the former is likely to undergo will involve a marked deterioration of the rubber, and sometimes even its complete ruin. In the above-described methods of analysis by solution, the proteid matter, being insoluble in rubber solvents, remains in the filtration-residue. Its detection and determination, however, are best carried out on the original rubber (*i.e.* on the washed sheet). For the determination Kjeldahl's method is employed, and it is usual to calculate by means of the usual factor 6·25 in converting nitrogen into proteid, although there is no direct evidence that this factor is strictly applicable.

VULCANISED AND MANUFACTURED RUBBER.

The rubber hydrocarbon readily combines with sulphur to form an addition-product; it is this which forms the basis of the great majority of manufactured rubber goods. The process by which this combination is brought about is known as "vulcanisation" or "curing"; there are two very distinct methods of vulcanisation, the "hot" and the "cold." According to the former, rubber is mixed with pulverulent sulphur and heated to such a temperature, and for such a time, as will lead to the result desired. Cold-curing consists in treating the surface of the rubber with a solution of sulphur chloride (S_2Cl_2) at ordinary temperatures, or exposing it to the vapours of sulphur chloride. Soft rubber goods are so vulcanised that there is comparatively little sulphur

combined with the rubber; that is, they are heated with a low percentage of sulphur to 120°-135°, or for very short periods of time to 170°-180°. Vulcanised soft rubber possesses at least as much tensile and shearing elasticity as raw rubber, and in addition it preserves these properties from low temperatures up to the point at which the rubber molecule begins to undergo decomposition. The properties of self-adhesion and plasticity are no longer found in rubber which has been vulcanised.

When rubber is mixed with a large quantity of sulphur and cured for a long time, or at comparatively high temperatures, the result is a quite distinct substance, ebonite; this is a horn-like solid which has still a certain shearing elasticity, but no tensile elasticity whatever.

Whilst raw rubber swells and dissolves in chloroform, carbon bisulphide, benzene, petroleum naphtha, and other solvents, the extent to which vulcanised rubber swells in these substances diminishes as the degree of vulcanisation increases, and becomes practically nil in the case of ebonite. Vulcanised rubber is remarkably inert towards chemical reagents; with a few exceptions, there is no reagent which attacks it, short of breaking down the rubber molecule completely.

For soft rubber goods or ebonites made of rubber and sulphur and nothing else, chemical analysis resolves itself into the determination of resin, combined sulphur, and free sulphur, possibly also of ash. Vulcanised rubber invariably contains some free sulphur over and above that which is combined with the rubber hydrocarbon. Free sulphur is soluble in boiling acetone, and is, therefore, extracted together with the resin by the method referred to on p. 425. The weight lost by the rubber on extraction represents resin plus free sulphur; the sulphur-content of the original minus the sulphur-content of the extracted material represents free sulphur. It should be noted that the proportion of resin to hydrocarbon in a rubber is apt to increase in the process of vulcanisation. For the determination of sulphur as such, see p. 419.

Soft rubber contains from 1 to 10 per cent. of combined sulphur, whilst ebonite contains 25-34 per cent. Manufactured rubbers containing intermediate percentages are also met with.

In vulcanisation by the cold-cure process both sulphur and chlorine enter into combination with the rubber hydrocarbon. The reaction takes place instantaneously, and rubber thus vulcanised does not permit of the further penetration of sulphur chloride; the cold cure can, therefore, be applied only to articles which have received their final shape, and of which only a thin superficial layer needs to be vulcanised. The commonest type of cold-cured goods are so-called cut sheet, and

composite articles made therefrom; this consists of sheet which is pared by knives from solid blocks of rubber. In addition, calendered sheet, proofed fabrics, and dipped goods lend themselves well to cold curing. The original cut sheet can always be recognised by the characteristic striæ arising from the action of the knife-blades; nowadays these marks are often artificially produced on calendered sheet by pressing the sheet on suitable fabrics, or, yet more simply, by the use of engraved rollers.

Dipped goods are made from solutions of clean unwashed rubber; the method applies especially to transparent articles. It is also possible to make seamless goods from mixtures of rubber solution with sulphur, and to heat-cure them after evaporation of the solvent.

Methods of vulcanisation other than the hot and cold cures are not in technical use. It is sometimes stated that certain metallic sulphides, e.g. those of antimony, alkalis, or lead, are vulcanising agents, but this is a fallacy. In reality it is the free sulphur associated with these sulphides which effects vulcanisation, the sulphides themselves acting merely as filters, or pigments, or conductors of heat. It may well be, however, that metallic sulphides play a part in vulcanisation as catalytic agents;[1] in many cases their presence seems indispensable to start the reaction.

B. ACCESSORY MATERIALS OF THE RUBBER INDUSTRY.

The principal raw material of the rubber industry has been dealt with in the foregoing section; numerous other substances are also used in making rubber goods.

Manufactured rubber seldom takes the form of pure vulcanised rubber without admixtures. This is mainly due to the fact that the purpose to which manufactured rubber is applied mostly call for something quite different from unmixed vulcanised rubber; filling materials are, moreover, largely employed for the sake of cheapness, and sometimes also with a view to producing deception.

In interpreting analytical results, therefore, the object with which the various ingredients have been added must be considered, and whether this may be regarded as useful, indifferent, or positively harmful, according to the nature of the case. The value and properties of rubber goods are very widely affected according to the nature and amount of the filling materials added. .

Few substances belonging to the domain of inorganic and organic chemistry have escaped the test of being incorporated in rubber mixings. A limited but still fairly large number have survived for

[1] Cf. *Gummi-Zeit.*, 1905, 19, 272.

normal or occasional use. The following are the more important filling materials:—

Inorganic Filling Materials.

Aluminium (in powder).	Lithopone.	Magnesia.
Iron (in powder).	Antimony Sulphide.	Magnesium Carbonate.
Zinc (in powder).	Kermes.	Magnesium-Aluminium Silicates (Fossil meal, Kieselguhr, Talite, Atmoid, Florida Earth, Meerschaum, Asbestos, Talc).
Brass (in powder).	Vermilion (Mercuric Sulphide).	
Litharge.	Ferric Oxide.	
Red Lead.	Cadmium Sulphide.	
White Lead.	Lime.	
Lead Sulphide.	Chalk.	Ultramarine.
Lead Sulphate.	Calcium Sulphide.	Clay of various tints.
Lead Chromate.	Calcium Sulphate, anhydrous.	Mica.
Zinc Oxide.		Glass powder.
Zinc Sulphide.		Pumice powder.
Barytes.	Calcium Sulphate, hydrated.	Various inorganic pigments.

Organic Filling Materials.

White Substitute.	Mineral Oils.	Graphite.
Brown Substitute.	Beeswax.	Earthy Lignite.
Fatty Oils.	Asphaltum (Bitumen).	Starch.
Lanoline.	Mineral Rubber (Acid-pitches and products of Mineral-pitches).	Dextrin.
Rosin (Colophony).		Potato meal.
Various Resins.		Plant fibres (Cellulose).
Rubber Resin.	Coal-tar Pitch.	Rubber Waste.
Resin Oils.	Resin Pitch.	Reclaimed Rubber.
Vaseline.	Petroleum and Lignite Pitch.	Viscose.
Ceresin.		Organic Dyestuffs.
Paraffin.	Lampblack.	

In most cases a rubber mixing contains not one but several of these ingredients, of which many are themselves of a composite character. Consequently the analysis of rubber goods, and especially the correct interpretation of analyses, is a matter of no small difficulty and requires considerable experience.

SUBSTITUTES.

By far the most important organic filling materials are a class of substances which owe their discovery and application solely to the requirements of the rubber industry, and are technically known under the name of "Substitute" (*Fr.* Factice, *Ger.* Faktis). There are two distinct kinds of substitute: white, and brown or black.

White Substitute is prepared by treating fatty oils, notably rape- and cotton-seed oils, with sulphur chloride, and forms loose, spongy, compressible aggregates or crumbs of a light yellow to white (rarely light brown) colour. The finest qualities, which, from the origin of

their manufacture, still sometimes go by the name of French substitutes, are made from castor oil. In recent times ready-dyed substitutes have been brought on the market. These latter are made by adding a soluble dyestuff to the oil before acting on it with sulphur chloride, in the proportion of 1 to 100 or 1 to 300, according to the tinctorial power of the dye.

The reaction which takes place when fatty oils are converted to solid "substitute" is much the same as that by which rubber is vulcanised with sulphur chloride. Chlorine and sulphur add themselves directly, though the details of the reaction are not as yet understood, to the glyceride molecule, or rather, to so much of the oil as represents unsaturated glycerides. The solid products contain in general 6-8 per cent. of sulphur, together with an equivalent amount of chlorine from which it follows that the absolute quantities of sulphur and chlorine present are approximately equal. Saturated sulphur-chloride addition-products are not soluble without decomposition in the ordinary organic solvents; but on treatment with alcoholic potassium or sodium hydroxide they behave exactly like normal glycerides and go into solution with formation of soaps soluble in water. In this process of saponification the chlorine is liberated almost completely, whilst the sulphur remains in combination with the fatty acid. Hence, by dissolving out a substitute by means of alcoholic potassium hydroxide and determining the sulphur in the fatty acid so obtained, the sulphur originally present in the substitute can be accurately ascertained. The chlorine of white substitute is altogether somewhat loosely attached; thus, when rubber mixtures containing white substitute are subjected to the heat-cure, a portion of the chlorine is liberated, probably as hydrochloric acid. White substitute, therefore, is not always a desirable ingredient in heat-cured goods. If, for instance, such mixings are spread on fabric and then heat-cured, the chlorine set free may act injuriously on the strength of the fabric, or even rot it completely.

Brown Substitute contains no chlorine, apart from traces. There are such preparations, however, as "mixed substitutes," which have been first treated with an inadequate proportion of sulphur and then finished off with sulphur chloride. Brown substitutes proper are made by heating fatty oils, as such or "blown" (*i.e.* oxidised), with sulphur alone to somewhat high temperatures; they thus bear the same relation to white substitutes as heat-cured to cold-cured rubber. They come into the market in the form of brown to black, moderately elastic, slabs or irregular blocks, or ground into crumby powder. Their sulphur-content is very variable, ranging from 3 to 18 per cent. Though otherwise insoluble, they are readily saponified with formation of sulphuretted fatty acids. The substitutes of commerce do not always consist exclusively of glyceride sulphides or chlorosulphides. They sometimes

contain inorganic admixtures, or paraffin wax or oil (as in so-called "Para français"), and usually a more or less considerable proportion of unchanged or incompletely vulcanised fatty oil. Apart from their application in connection with rubber, they are now used for making pencil erasers and the like, consisting of nothing but substitute with mineral fillers.

The chemical examination of substitutes is important. Substitutes which have been insufficiently or negligently vulcanised, or those which have been vulcanised from imperfectly boiled oils, may seriously impair the keeping qualities of rubber goods in which they form an ingredient. A good substitute should contain little or no free sulphur, and not more than 3 per cent. of ash; nor should it contain any considerable quantity of mineral oil or paraffin wax, unless it be of the type in which a definite admixture of this kind is known and allowed for. Thus the "Para français" type of brown substitute always contains 15-20 per cent. of paraffin wax, and sometimes as much as 40 per cent. In analysis, free sulphur, unchanged or incompletely vulcanised fatty oil, and petroleum derivatives are separated by extraction with acetone, and weighed together. Hydrocarbon oils and waxes are isolated, after saponification, according to the method described in the Section on "Lubricants," this Vol., p. 89. Total chlorine and sulphur in white substitute, and total sulphur in brown substitute, are determined in the same way as in rubber goods (cf. infra, p. 419). Chlorine and sulphur may be determined in one and the same sample by adding a little silver nitrate to the nitric acid with which the material is decomposed; any chlorine which might otherwise escape is thus retained from the outset. The Carius method is not to be recommended.

To obtain a more complete knowledge of the nature of a substitute, the saponifiable portion of the acetone-soluble matter may be assayed for sulphur, and its iodine value may be determined, and also the iodine value of the saponifiable portion of the residue from acetone extraction.

The scheme of analysis is as follows :—

1. Extraction of 2-4 g. with acetone in a Soxhlet or Zuntz apparatus. Both extract and residue are examined for unsaponifiable matter by the Spitz and Hönig method, and this, if present, is identified as far as possible. In the isolated fatty acids combined sulphur is determined, and, if desired, the iodine value.

2. Determination of total sulphur and chlorine.

3. Incineration and examination of the ash.

4. Determination of saponifiable and unsaponifiable matter in the original material, and of sulphur, iodine value, and saponification value in the saponifiable portion. In most cases this procedure replaces, and is to be preferred to, that given under 1.

Definite standards for the valuation of substitutes cannot well be set up. The following qualitative tests, supplemented by analyses 2 and 3, are useful for differentiating good substitutes from bad :—

a. On shaking with 20 parts of cold water, only the faintest acid reaction with Congo red paper should be produced.

b. On digesting at 50°-60° for half an hour with 20 parts of 96 per cent. alcohol, silver nitrate should give only a faint opalescence after an hour or so. The alcoholic extract, after cooling, filtering, and evaporating, should leave a residue amounting to not more than 0.4 per cent. of the substitute.

c. On heating for an hour to 100°-110°, there should be no perceptible change and no evolution of acid vapours. This applies more especially to dry white substitutes.

d. On heating for one to four hours in a sealed tube to 150°, there should be no evidence of pressure or of acid vapours when the cooled tube is opened.

OTHER ORGANIC ACCESSORIES.

Apart from substitutes, the chief organic filling materials are :— Bitumen, tar, pitch, mineral oil, paraffin wax, ceresin, beeswax, fatty oils (especially in admixture with reclaimed rubber), rosin oil, resin, lanoline (rarely used), and the other substances enumerated on p. 410. Details as to the examination of each of these are given in the Sections concerned with the respective substances. The most important condition for the applicability of pitchy, oily, and similar materials is that they should be completely free from moisture. The following special points may be noted :—

Bitumen.—In rubber mixings only bitumens of superior quality, obtained from the mineral by liquation or extraction, should be employed. The most suitable bitumens are those which have a softening point (as determined by Krämer and Sarnow's method ; see Section on " Coal Tar," Vol. II., Part II., p. 837) of not less than 30°-35°. The comparatively rare varieties which soften about 50° and contain a good deal of combined sulphur are particularly prized. Bitumens are partially soluble in boiling acetone.

Pitch.—Coal-tar pitch is largely used in the manufacture of goloshes and other goods, and is generally prepared on the spot by boiling down tar. It usually has a softening point of 52° or over. In the boiling down a certain amount of pulverulent carbon is produced, the total quantity of which may amount to 15-35 per cent. ; it is, therefore, desirable that the original tar contain as little carbon as possible, and that excessive local heating of the boiling-pans be avoided. For the determination of pulverulent carbon, see Section on " Coal Tar," Vol. II.,

Part II., p. 759. When rubber goods containing pitch are analysed, this carbon appears as lampblack, and cannot be distinguished from intentionally added lampblack. A portion of the pitch is soluble in acetone. From these facts it follows that an accurate determination of pitch in rubber goods is impracticable. Approximate data can be obtained by extraction with pyridine or with ethyl acetate.

Solvent Naphtha.—The benzene homologues derived from coal-tar are much in use as rubber solvents. Only the most highly purified naphthas are admissible in rubber manufacture; they must not impart the slightest odour to the rubber from which they have evaporated. Methods of examining coal-tar naphthas are given in the Section on "Coal Tar," Vol. II., Part II., pp. 779 et seq. The varieties in common use are the benzene, toluene, and xylene fractions. Of a solvent naphtha not less than 95 per cent. should distil over up to 155°.[1]

Shale Spirit.—This solvent is prepared from the products of destructive distillation of bituminous shale, and generally begins to distil at about 80°; it should distil over completely below 140°. Shale spirit consists of benzene, paraffin hydrocarbons, and naphthene hydrocarbons in varying proportions.

Petroleum Naphtha.—Paraffin hydrocarbons are used as rubber solvents, and as diluents of sulphur chloride in the cold-cure; for the latter purpose, however, they are not so good as benzene, and far less effective than carbon bisulphide. In selecting the most suitable fraction, it should be noted that very low boiling points involve much loss by evaporation, and that such naphthas are relatively poor solvents for rubber. On the other hand, heavy naphthas are even more to be avoided, since they impart a tenacious odour to rubber goods, and are liable to soften the rubber under the influence of heat. The most useful petroleum naphthas are those of which 95 per cent. distils between 100° and 140°.

Reclaimed Rubber.—An ingredient of manufactured rubber goods which is now used in enormous quantities, is used-up rubber scrap which, by various processes, has been rendered fit to be incorporated in fresh mixings. The chemical examination of this article, which is not easily valued by inspection, is of considerable importance.

In the first place the ash, or preferably the true mineral constituents, should be determined both qualitatively and quantitatively. The acetone extract should also be similarly examined. Reclaiming processes convert the substitutes originally present into acetone-soluble matter to a large extent. Free sulphur is rarely present in appreciable quantity, but, if it is, the sulphur-content should be accurately known. The kind of reclaimed rubber which is prepared by plasticising ground rubber waste with much mineral or rosin oil suffers in value by the

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[1] For further details, cf. *Gummi-Zeit.*, 1903, 17, 793.

presence of these additions, and by the fact that it contains a relatively high proportion of ash to true rubber. It is frequently possible to recognise the particular reclaiming process which has been applied, as when the presence of alkali or of acid, or of certain solvents, is detected. Generally speaking, the examination of reclaimed rubber is conducted similarly to the analysis of rubber goods. In many cases the nitrosite or tetrabromide method serves for determining the amount of true rubber present. The acetone extract may contain, beside oils, resins, etc., certain decomposition-products of rubber which somewhat resemble paraffin hydrocarbons; these may be recognised, quantitatively at least, by the formation of insoluble bromides similar to rubber tetrabromide.

Organic Colouring Matters.—Of these the representatives are lake pigments and those dyes which, being insoluble in water, but soluble in oils or naphthas, are applicable to cold-cured goods. They should be assayed for ash, and further examined qualitatively by the methods in use for dyes; the most trustworthy information is to be obtained by spectroscopic methods.

Fabrics intended to be impregnated with rubber should be free from sizing; they should, moreover, be tested for the presence of copper, which sometimes occurs in dyed fabrics as a mordant, and has an injurious effect on vulcanised rubber, especially on long standing. It may also be necessary to determine the number of threads in unit area, the weight per unit area, and the tensile strength. In balloon fabrics the important points are proper mode of weaving and adequate protection of the exposed side, by means of pigments, from the sun's rays.

INORGANIC ACCESSORIES.

Sulphur.—This, of all rubber accessories, is the one used in greatest quantity. For the examination of sulphur, see Vol. I., Part I., p. 264. The principal desiderata from the standpoint of the manufacture of rubber are, freedom from moisture and acidity, and a high degree of fineness.

Sulphur Chloride.—Uniformly good results in the cold-cure are only to be obtained with very pure sulphur chloride. The presence of dichloride, that is, excess of chlorine, produces a harsh, shrivelled surface on the goods, whilst free sulphur, which is frequently present in considerable quantity, causes the goods to "sulphur up." The latter impurity is the less noxious of the two, and may be tolerated to the extent of 3-5 per cent. The following method of analysis is prescribed by Weber:—

From 20-30 g. of sulphur chloride are weighed by difference out of a small stoppered bottle into a litre flask half filled with water. The flask is stoppered and shaken until there are no more oily drops, and

is then warmed for a short time on a water-bath. For every 1·0 g. of sulphur chloride 1 c.c. of nitric acid (sp. gr. 1·42) is added. The liquid is cooled, made up to the mark, and filtered through a dry pleated filter. The chlorine is determined either gravimetrically or volumetrically in an aliquot portion of the filtrate. The excess of chlorine or of sulphur present may be calculated from the content of chlorine.

Antimony Sulphide.—The red antimony pigment used in the rubber industry always contains more or less free sulphur; even the purest form obtainable contains about 8 per cent. as an inevitable consequence of the method of manufacture. A wide variety of antimony sulphides is supplied by the makers, differing in the content of free sulphur (e.g. 8, 15, 20, 25, etc., per cent.) intentionally added; these are commonly sold on a guarantee of a definite sulphur-content. The ratio of combined sulphur to antimony in commercial sulphides is apt to vary, as is shown in the subjoined analyses :—

	A.	B.	C.	D.	E.	Laboratory Preparations (Henriques).	
SiO_2	2·85	...	0·60	1·56	...	...	...
$CaSO_4$ . . .	15·45	3·38	6·55	14·33	...	...	...
Free S	17·10	8·55	11·06	24·00	40·06	8·10	8·80
Sb	44·03	61·28	53·54	41·53	40·30	58·24	58·84
S combined with Sb . .	19·97	27·57	27·91	18·30	19·09	33·47	32·36
Sb_2S_5	16·54	21·84	43·18	13·64	20·45	66·66	58·14
Sb_2S_3	47·46	67·01	38·27	46·19	38·94	25·05	33·06

Free sulphur is determined by extracting a weighed sample, dried at 50°, in a Soxhlet tube with carbon bisulphide. The powder is placed in a Schleicher and Schüll paper thimble, which is weighed in a stoppered weighing-bottle before and after extraction. The further analysis may be carried out according to the following method, due to F. Jacobsohn : [1]—

For the estimation of the total sulphur, the substance is evaporated in a dish with concentrated nitric acid; the residue is cautiously treated with fuming nitric acid, and again taken to dryness. After lixiviation with hot water, the sulphur is determined as barium sulphate in the usual manner.

Antimony is determined as the oxide, SbO_2, together with any other mineral matter present. This is done by oxidising the extracted sulphide with fuming nitric acid, taking to dryness, and igniting.

The separation of antimony from other mineral constituents is effected as follows :—The oxidised residue obtained as above is mixed

[1] Chem. Zeit., 1908, 32, 984 ; J. Soc. Chem. Ind., 1908, 27, 169.

with ammonium chloride and again ignited. By this means the antimony is volatilised away, whilst other mineral matter remains unaffected. If there is any calcium present as antimoniate or sulphantimoniate, an error is thereby introduced, but this is generally very small.

The more exact analytical separation is carried out by evaporating the sulphide with hydrochloric acid, oxidising with a drop or two or nitric acid, dissolving in dilute hydrochloric acid with a little tartaric acid, filtering off the silica, and precipitating the antimony with sulphuretted hydrogen. The antimony sulphide is weighed and the calcium determined in the filtrate as usual.

Vermilion.—This is the most brilliant of red rubber pigments, and has the greatest covering power. It is met with in several shades, but invariably consists of practically pure mercuric sulphide, unless adulterated. Sometimes small quantities of insoluble aniline dyes are added to enhance the colour. These may be isolated by extraction with ether, and duly identified; usually they are dyes of the azo- or eosine series. Adulteration with aniline dyes, however, is very seldom practised. It is well to test for soluble mercury salts, since rubber goods pigmented with vermilion are often used in contact with beverages or foodstuffs.

Covering Power is determined by mixing a little of the material with oil, spreading on a clean dry glass plate, and making comparative tests.

The organic and inorganic compounding materials not dealt with above call for no special comment. Methods of analysis in each case will be found in other Sections. For the rubber industry, fineness of division, dryness, and freedom from acidity are indispensable.

C. THE ANALYSIS OF RUBBER GOODS.

It will have been gathered from the foregoing that manufactured rubber articles may be—and mostly are—composite substances of the greatest complexity. The various non-rubber ingredients being generally impure chemicals, or themselves of a composite nature, it is seldom possible to estimate them accurately by analysis; all that can be done, in the first instance, is to determine the elements or simple compounds present in the sample. Moreover, the variety of raw rubber originally employed is hardly ever to be diagnosed with certainty from the results of analysis. Hence the correct interpretation of a complex analysis is largely a matter of experience, for which a scheme of general applicability cannot be drawn up. Some general notes in this connection are given in the last paragraph of this Section (p. 435).

III   2 D

SPECIAL METHODS OF ANALYSIS.

1. Preparation of the Sample.

To counteract possible lack of homogeneity resulting from the methods of manufacture, it is well to begin by taking a fairly large quantity of material and preparing an average sample. This may best be done by reducing the rubber to a state of powder.

Stiff rubber goods and ebonites can quite easily be powdered by means of a rasp or file. The softer kinds of goods, *e.g.* sheeting and tubing, can be similarly comminuted by tying them up in tight rolls and applying the file at right angles to the axis. Unvulcanised goods, cut sheet, and very thin sheeting or proofing cannot be treated in this way; in this case the material is kneaded or crumpled together, and narrow strips are cut out in diagonal directions. The recommendation is often made to reduce the material to crumb on a small pair of rollers. This, however, is a questionable procedure, because vulcanised rubber is apt to be altered, on mastication, by a partial de-polymerisation of the rubber molecule, the consequence being that its conditions of solubility and thence the analytical results, are more or less affected.

A grinding apparatus, consisting of two solid grooved gun-metal rollers, for the preparation of vulcanised rubber for analysis, has been recently described by L. Archbutt.[1]

2. Desiccation.

The drying of rubber is an analytical operation which recurs frequently and calls for special care. The best method is to weigh the rubber in a porcelain boat, place the boat, or several boats, in a glass tube heated to 80°-95°, and pass a continuous current of hydrogen or carbon dioxide through the tube. In this way all danger of oxidation is avoided. Drying can also be conducted in a vacuum oven, the precaution being taken to allow the oven to cool down before opening; this method permits of working at low temperatures, but is not without its disadvantages. Drying in a current of coal gas is much practised, but is not to be recommended, because rubber has a tendency to absorb hydrocarbons out of the gas. The risk incurred in drying in an ordinary oven at 90°-95° is that rubber, especially vulcanised goods with much filling, invariably undergoes some slight oxidation in the process; nevertheless this method is much the simplest, and, in cautious and experienced hands, gives quite acceptable results.

[1] *Analyst*, 1913, 38, 550.

3. Incineration.

Formerly the chief weight was laid on the percentage of ash in all rubber analyses. The ash, indeed, always corresponds approximately to the sum of the mineral constituents present. There are, however, numerous possible sources of error; thus carbonates and sulphates may undergo more or less decomposition, oxides may combine with sulphur, and volatile metallic compounds may be driven off. The ash of filled rubber goods, therefore, cannot be regarded as an accurate index of the proportion of filling material. It should always be determined, however, because it serves as a check on the inorganic part of the analysis, and it may also be needed as an auxiliary factor in the determination of substitute. To determine the ash, about 0·5 g. is weighed into a flat porcelain dish of about 5 cm. diameter. The dish is placed on a hole of 3-4 cm. diameter cut in a piece of metal or asbestos sheet, and is gently heated in such a way that the rubber substance fumes off without taking fire. If the rubber is allowed to burn, there is always a considerable deposition of soot, which has to be removed by vigorous ignition; and not only is time thus lost, but the ash may undergo further decomposition than is necessary. Carefully performed incinerations take from ten to twenty minutes, and can be carried out at temperatures which leave most of the carbonate present undecomposed. Finally, the ash is weighed, and may serve for a qualitative analysis of the mineral matter.

When the rubber contains no fillers, the ash represents the mineral impurities present in the original rubber; these, even in well-washed rubbers, always amount to several tenths of a per cent., and in some varieties even to several per cent.

4. Total Sulphur.

Four methods for the estimation of sulphur are given of which the one under (b) may be especially recommended. It demands more care than Method (a), but saves a good deal of time.[1] A method for the estimation of free sulphur, which is contained in the acetone extract, is described on p. 438.

Method (a).—About 1 g. of the comminuted sample is weighed into a small lipped beaker and is treated with 15-20 c.c. of pure concentrated nitric acid (sp. gr. 1·4). The beaker is covered with a perforated watch-glass and slowly warmed on a water-bath. A brisk reaction, which should not go so far as to cause spirting, takes place and lasts for about an hour. At the end of this time the contents of the beaker are

[1] Methods (a) and (b) are modified forms of Henriques' method, *Z. anal. Chem.*, 1899, 12, 802.

rinsed with strong acid into a small porcelain basin of about 5 cm. diameter and evaporated to dryness. A short length of glass rod is used from the beginning for pushing and stirring, and is eventually allowed to remain in the dish. The substance is subjected to two more evaporations with about 3 c.c. of nitric acid. When it has been brought to a syrupy consistency, it is moistened with a few drops of alcohol and mixed, whilst still warm, with about 5 g. of finely powdered sodium carbonate and potassium nitrate in the proportion of 5 parts of the former to 3 of the latter. The magma is covered with a layer of the same mixture and is dried at 120°-130°. Now follows the critical stage of the analysis, namely, the fusion, in which very great care must be exercised to avoid sudden decompositions having the character of a mild explosion. The basin is supported about 5 cm. above a small luminous Bunsen flame which is increased little by little, a second similar basin being placed, mouth downwards, upon it. At first it may be necessary from time to time to wipe away condensed moisture from the covering basin. Should an explosive reaction presently take place, the spatterings are taken up by the covering basin and are afterwards fused in it by themselves. Under proper conditions, however, the mass gradually turns brown at the edges and can then be heated with more confidence, the brown matter which condenses on the cover being free from sulphur. Finally, the contents of the basin are brought into complete fusion, and are stirred with the glass rod mentioned above, which is held in a pair of tongs. The fusion occupies from one and a half to two and a half hours.

Special basins[1] with a thin glaze inside only are supplied for this fusion. In lixiviating, it is best not to cool down the melt completely, but to add hot water whilst it is still warm. The basin having been rinsed clean, the insoluble residue (mainly oxides and carbonates) is filtered off and washed until the runnings no longer give a reaction for sulphates.

In the clear filtrate there will be an appreciable quantity of silica only if the rubber itself contains much siliceous matter; on this point a qualitative examination of the ash will have supplied information. It will then be necessary to acidify, take to dryness, redissolve, and filter. The total sulphur is then precipitated and weighed in the usual way as barium sulphate. There being an excess of nitrates present, it is advisable to wash the precipitate with hot, dilute hydrochloric acid. In the case of ebonites or soft goods heavily loaded with sulphides and sulphates, an aliquot part of the filtrate, rather than the whole, should be taken for precipitation.

The insoluble residue on the filter can be made use of for determining the mineral filling materials of the rubber, since it contains

[1] Made by Haldenwanger & Co., Charlottenburg.

practically all of the metals concerned in the form of oxides or carbonates. Negligible quantities of lead and calcium may go into the filtrate, and sufficient antimony to be worth precipitating with sulphuretted hydrogen in the final liquor filtered from the barium sulphate. The insoluble residue is then treated with hydrochloric acid, when only silica remains behind, and the resulting solution is subjected to the usual course of quantitative analysis. The only metal which cannot thus be determined is mercury, most of which escapes during the fusion. Certain superior qualities of red rubber goods contain vermilion ; in this case mercury must be determined by itself in a separate portion of the sample. The same procedure, may with advantage be applied to antimony (cf. *infra*, p. 427).

Method (b).—About half a gram of comminuted rubber is weighed directly into a small basin and allowed to stand for an hour with 2-3 c.c. of concentrated nitric acid. The basin is then placed on a cold water-bath, which is gradually heated up; in this way a too violent reaction between the rubber and the acid is avoided. The first portion of acid having been evaporated, 5 c.c. of fuming nitric acid are added, and from this point onwards operations are conducted exactly as under Method (*a*).

Method (c).—The familiar Carius method, as adapted to rubber, is carried out as follows:—From 0·5-1·0 g. of rubber are weighed into a very small test tube and placed in a tube of special glass, into which 3-5 c.c. of fuming nitric acid have previously been poured. The open end of the tube is then drawn out to a capillary in the usual way, and sealed. By inclining the tube the acid is very gradually and cautiously brought into contact with the rubber; during this operation the tube must be held in an iron mantle or well wrapped in cloths, since there is some risk of explosion, especially with rubber of low vulcanisation or containing substitute. After cooling down for an hour or so the pressure is released and the tube re-sealed ; it is then heated to about 200° in a tube-furnace. The final product will consist not only of a liquid but also of a solid sediment which may contain sulphates ; the whole is, therefore, rinsed into a basin, evaporated, and fused with potassium and sodium carbonates. The melt is dealt with as under Method (*a*), and serves for the determination of the total sulphur and of the mineral ingredients.

Method (d).—It has been proposed to use v. Konek's process, by which the rubber is decomposed with sodium peroxide for the determination of sulphur in rubber. In some cases it is possible to determine the sulphur, as sulphate, volumetrically by the method of J. D. Pennock and D. A. Morton.[1]

[1] *J. Amer. Chem. Soc.*, 1903, **25**, 1265 ; *J. Soc. Chem. Ind.*, 1904, **23**, 131. For details of the whole process, see Alexander, *Gummi-Zeit.*, 1904, **18**, 729.

5. Chlorine.

Any chlorine present in rubber goods is practically always in organic combination. To determine it, 1 g. of rubber is cautiously fused with a mixture of sodium carbonate and potassium nitrate; no volatilisation of chlorine need be feared. The melt is dissolved in water acidified with nitric acid, and the chlorine determined either volumetrically or gravimetrically. The fusion-mixture should always be tested, not only for chloride but also for chlorate.

In unvulcanised or heat-cured goods the presence of any appreciable quantity of chlorine points to the presence of white substitute. The latter generally contains from 6-8 per cent. of chlorine, so that its approximate amount in the rubber may thus be calculated. In cold-cured goods free from white substitute the chlorine is present as a vulcanising agent, and forms part of the sulphur chloride taken up in the cure. Should substitutes be present, it is necessary to separate them by extraction with alcoholic potassium hydroxide, and so to differentiate between the sulphur and chlorine belonging to the rubber and the substitute respectively.

6. Sulphur Combined with Metals.

Sulphur may be present in inorganic combination in the form of (a) sulphides or (b) sulphates.

(a) *Sulphur in the form of Sulphides.*—To determine sulphides, the rubber is boiled with hydrochloric acid until sulphuretted hydrogen can no longer be detected in the vapours. The rubber is then dried and the contained sulphur determined. The difference between the sulphur so found and the total sulphur gives the sulphide-sulphur. There is seldom, however, any need to carry out this determination. Lead sulphide, which is often present in rubber, will have rarely been added as such, but is produced by the reaction of sulphur on litharge in vulcanisation. Sulphur combined with antimony, in red rubber goods, may be calculated from the antimony present on the approximately correct assumption that the sulphide is Sb_2S_4 (see above, p. 416). Similarly, sulphide-sulphur may be present as HgS (vermilion) or as ZnS (in the form of lithopone).

(b) *Sulphur in the form of Sulphates.*—The only sulphates commonly used as fillers are those of barium and calcium. If barium is present, and if on boiling the rubber with dilute hydrochloric acid no barium goes into solution, the metal is present wholly as the sulphate, and the combined sulphur can be calculated from the barium. To determine calcium sulphate, a weighed quantity of rubber is thoroughly boiled out

with hydrochloric acid and the dissolved sulphate precipitated in the usual manner. Any other sulphates present in small quantity will have been formed in vulcanisation, or have been introduced by reclaimed rubber.

7. Carbonic Acid.

Among the commonest inorganic fillers are carbonates, especially those of calcium, and, in minor degree, those of lead, zinc, and magnesium. The estimation of these carbonates, in presence of the corresponding oxides, is effected by decomposing 1 g. of rubber with dilute phosphoric or hydrochloric acid in any of the well-known forms of apparatus, and determining the carbon dioxide liberated by loss. To prevent loss of sulphuretted hydrogen evolved from sulphides, the rubber is in the first instance moistened with copper sulphate solution to which 50 per cent. of alcohol (to overcome surface tension) has been added. The method can be employed only with material in the form of tolerably fine powder, and is useless for unvulcanised rubber or for goods which are too soft to be disintegrated to dust.

Generally speaking, the determination of sulphides (Method 6) and of carbonates in the rubber itself is best circumvented by isolating the mineral fillers as described below (Method 8), and carrying out these determinations on the pulverulent material so obtained.

8. The Direct Isolation of Filling Materials.

(a) *Frank and Marckwald's Method*.[1]—The rubber is comminuted and submitted to acetone extraction. Of the dried residue 1 g. is placed together with 30 c.c. of xylene in a wide test tube of thick glass with a ground-in stopper. Four or six of these may be charged at once; they are set up in a metal stand and placed in an autoclave containing xylene. There must be sufficient xylene in the autoclave to obviate any risk of going to dryness; it may with advantage be half filled. The autoclave is closed and heated up in the course of an hour to a pressure of 15 atmos. The pressure is then kept at 15-18 atmos. during three or, to make sure, four hours. The autoclave is then allowed to cool down, blown off, and opened. If the solid matter in the tubes has settled and left the liquid clear, an equal volume of ether is added and gently stirred in. If the liquid is turbid, 1-3 c.c. of absolute alcohol are added, whereby a slight precipitation of rubber is brought about, and the liquid is effectually cleared; it is then diluted with ether as before. The tubes are allowed to stand overnight. The solid matter is then collected on a weighed filter and washed well with ether, which removes

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[1] *Gummi-Zeit.*, 1908, 22, 134.

any precipitated rubber; it is then dried and weighed. This solid matter, which consists of inorganic fillers, carbon, fibres, and mechanical impurities, should be a dry, impalpable powder; lumps of rubber, if present, are either removed by a suitable solvent or separated and allowed for in the subsequent analytical operations. One portion is taken for the determination of total sulphur. Another portion is analysed as follows :—By warming with dilute, followed by concentrated, hydrochloric acid, carbonates, sulphides, etc., are removed; the residue is re-weighed. The constituents soluble in acid may be determined in the usual way. On igniting the insoluble residue, the loss gives the carbon and other organic matter. The ignition-residue is dealt with by the ordinary procedure of quantitative analysis. This separation into acid-soluble, organic, and refractory constituents greatly facilitates the interpretation of the analytical data. Further portions of the original material may be used for the determination of carbonic acid and sulphide-sulphur.

It is to be noted that when red rubber goods containing vermilion are to be dissolved by this method, the rubber and xylene must be heated up in sealed tubes. If the tubes are open, mercury will escape by volatilisation, and may cause serious damage to the autoclave.

(b) *F. Hinrichsen and W. Manasse's Method.*[1] — The rubber is brought into solution by heating at atmospheric pressure with petroleum, a solvent originally proposed by Henriques.[2] 1 g. of the acetone-extracted and dried material is placed in a 100 c.c. conical flask, together with 25 c.c. of a petroleum fraction distilling between 230° and 260.° Frank and Marckwald[3] suggest liquid paraffin of sp. gr. 0·86. The flask is heated under a reflux condenser, by means of an air-, paraffin-, or sand-bath, but not to ebullition of the solvent. Some rubbers go into solution at 120°-130°, others require temperatures of 180°-200°; fumes of white vapour are a sign of over-heating. When, after an hour or two, no more undissolved rubber can be observed, the flask is allowed to cool and the contents diluted with petroleum spirit. The solid matter is separated, not by filtration, but by the use of a centrifugal machine. After the flask has been whirled for about half an hour at a speed of 1500 revolutions per minute, the sediment will generally have settled so firmly that the supernatant liquid can be simply poured off. Fresh petroleum spirit is then added, boiled up with the solid matter, whirled and poured off as before; the operation is repeated once or twice. Finally, the solid residue is dried at 105° and weighed. It is analysed as under Method 8 (a).

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[1] *Chem. Zeit.*, 1909, **33**, 735 ; *J. Soc. Chem. Ind.*, 1909, **28**, 843.
[2] *Chem. Zeit.*, 1892, **16**, 1624.   [3] *Gummi-Zeit.*, 1909, **24**, 213.

9. Extraction with Volatile Solvents.

The most common, though not the only, solvent currently employed in rubber analysis is acetone. With a homogeneous solvent such as this the best extractor to use is that of Zuntz, with a mixture, that of Soxhlet; modifications of both forms of apparatus have been designed with special reference to rubber analysis (see p. 400). With solvents of high boiling point (above 80°-100°) it is better to carry out the operation by simply boiling under a reflux condenser rather than with the aid of an extractor. The boiling-vessel connected with the extractor may be either a conical flask or the wide-mouthed Soxhlet flask. Several extractors may with advantage be set up together on a stand such as that shown in Fig. 55.

Pulverulent materials are placed in a filter-paper thimble; cuttings of sheet are rolled up upon muslin, as described on p. 400. Extraction is continued for six to ten hours, and its completion is gauged by taking a sample of the solvent out of the extractor and evaporating. The liquid in the flask is then distilled off and the residue dried and weighed.
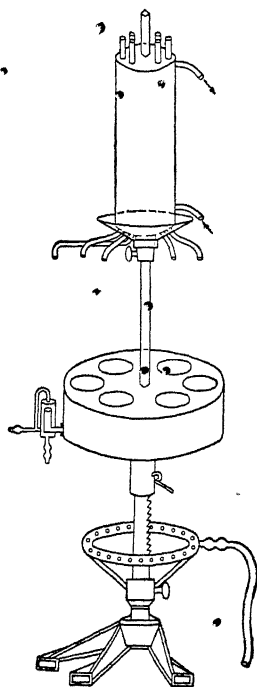
FIG. 55.

10. Determination of Substitutes.

As will be gathered from what was said about substitutes on p. 411, these are determined by extraction with alcoholic potassium hydroxide. About 5 g. of acetone-extracted material are boiled for four hours under a reflux condenser with 25 c.c. of semi-normal alcoholic potassium hydroxide. The liquid is poured off, the residue washed out with boiling water until no alkaline reaction can be detected, and then dried on a watch-glass or in a weighing bottle. The difference in weight before and after extraction represents the saponifiable matter. It is to be noted, however, that in this way something less than the percentage of substitute originally incorporated will always be found, because the previous extraction with acetone will have removed the unvulcanised oily portion of the original substitute. On the other hand, the difference in weight is itself liable to a plus error, owing to the removal of some of the mineral matter (antimony sulphide, zinc oxide, silica) by the alkaline liquors.

In the case of unvulcanised doughs the direct action of alcoholic potassium hydroxide is inapplicable, since the material would be only superficially attacked, and it is necessary to proceed as follows:— 5 g. of substance and 25 c.c. of benzene are warmed for an hour under a reflux condenser on a water-bath and allowed to stand overnight. By this time a thick solution will have been formed which offers no resistance to the action of alcoholic alkali; it is boiled for four hours with 25 c.c. of semi-normal alcoholic potassium hydroxide as above. Both the alcohol and benzene are then completely distilled off, and the residue freed from substitute-soap, etc., by repeatedly boiling out and kneading with hot water.

As an alternative to determining substitute by the loss of weight of the rubber, the fatty acids of the substitute may be directly isolated and weighed. For this purpose the alcoholic potassium hydroxide solution is freed from solvent by evaporation, combined with the aqueous washings, and acidified. The fatty acids are then extracted with ether and weighed in the usual manner.

11. Resins Insoluble in Acetone.

A number of resins are in use as ebonite ingredients which cannot be completely extracted by means of acetone, and are, indeed, very resistant to organic solvents generally. C. O. Weber[1] proposes to deal with these by an extraction with epichlorhydrin, following immediately upon the acetone extraction. The following data as to solubility are adduced by Weber :—

	Acetone.	Epichlorhydrin.
Copal	Partially soluble	Soluble
Dammar	,,	,,
Mastic	,,	,,
Sandarac	Soluble	Partially soluble
Shellac	Insoluble	Soluble

12. Pitch and Bitumen.

A portion of these materials always goes into solution in the acetone extraction. For detecting the presence of pitch, pyridine is a useful solvent, but it attacks rubber; for this and other reasons it cannot be made use of with advantage for quantitative work. Generally speaking, it is impossible to determine admixtures of this class with any great accuracy. Sometimes ethyl acetate, following upon acetone,

[1] *The Chemistry of India Rubber*, p. 260.

gives good results. In the absence of added lampblack, an indication of the presence of coal-tar pitch, and an approximate estimation, is afforded by the presence of pulverulent carbon in the rubber.

Carbon bisulphide has been proposed as a solvent by R. Becker.[1] The acetone-extracted material is treated for one hour in a Zuntz extractor with carbon bisulphide. Owing to its low boiling point, this solvent is stated to take up no appreciable quantity of rubber, provided the extraction be not unduly prolonged.

13. The Direct Determination of Antimony and Mercury Sulphides.

When it is desired to determine these pigments alone in a red rubber or ebonite, it is best to destroy the rubber and other organic matter by means of drastic reagents. This can be done by either of the following methods[2] :—

(a) *Method of F. Frank and K. Birkner.*[3]—Half a gram of comminuted rubber is put into a round-bottomed 100-150 c.c. flask together with 10 g. of ammonium persulphate, and 10 c.c. of fuming nitric acid are added. These proportions, which have been worked out by experiment, should be adhered to as far as possible. A vigorous reaction takes place during a few minutes, whereupon the flask is heated on a sand-bath. After fifteen to twenty minutes the evolution of gas will have ceased. If now there remain particles of undecomposed organic matter, 2-3 g. of ammonium persulphate are gradually added during ten minutes or so; this quantity is certain to suffice. Any nitric acid which may still be present is then boiled off; but excessive heating should be avoided, since insoluble metallic compounds may thereby be formed. The clear melt is allowed to cool until crystallisation sets in. Before solidification has gone too far, 10 c.c. of hydrochloric acid (sp. gr. 1·124) are added, and the solution is diluted with warm water. The insoluble mineral matter is filtered off, the filtrate further diluted, and the antimony and mercury are then precipitated by means of sulphuretted hydrogen. In the ordinary way, the two sulphides,—in case antimony and mercury are both present,—may be collected, washed with carbon bisulphide, dried, and weighed together; antimony is then dissolved out with ammonium sulphide, and the residue is again treated with carbon bisulphide, dried, and weighed. Should a greater degree of accuracy be desired, the two metals must be separated by more refined methods of quantitative analysis.

(b) *Method of W. Schmitz.*[4]—In this method, which was primarily

[1] *Gummi-Zeit.,* 1911, **25**, 598.
[2] *Cf.* also Rothe, *Chem. Zeit.,* 1909, **33**, 679.
[3] *Chem. Zeit.,* 1910, **34**, 49; *J. Soc. Chem. Ind.,* 1910, **29**, 224.
[4] *Gummi-Zeit.,* 1911, **25**, 1928; *J. Soc. Chem. Ind.,* 1911, **30**, 1223.

worked out for antimony alone, the organic matter is destroyed, as in Kjeldahl's method for the estimation of nitrogen. From 2-4 g. of comminuted rubber, together with 13-15 c.c. of concentrated sulphuric acid for each gram, are placed in a long-necked, 300 c.c. flask; a drop of mercury weighing about 0·1 g. and a small piece of paraffin wax are added, and the flask is heated on a sand-bath until the contents form a homogeneous liquid and begin to lighten in colour. After cooling, from 2-4 g. of potassium sulphate are introduced, and the heating is continued to decolorisation. On adding water to the cooled liquid most of the mercury is precipitated as a white powder. Tartaric acid is then added and a gram or two of potassium metabisulphite (to reduce the mercury); the liquid is copiously diluted, boiled till free from sulphur dioxide, a little hydrochloric acid added, and then filtered. The determination of the antimony may be effected either gravimetrically or volumetrically in the filtrate.

14. The Direct Determination of Rubber.

Many methods and modifications of methods for the determination of rubber in vulcanised articles by the nitrosite or tetrabromide process have been proposed. The two following methods are to be depended upon so far as they go, but, at best, they yield only approximate results.

(a) *P. Alexander's Nitrosite Method.*[1]—Half a gram of comminuted and acetone-extracted rubber is suspended in carbon tetrachloride, and allowed to swell during some hours, or, better, overnight. It is then treated with nitrous gases in the same manner, and with the same apparatus, as for crude rubber (see above, p. 403). The nitrosite is formed even more readily than from crude rubber. After standing overnight in the liquid saturated with red gases, the fragments of rubber will generally have been completely converted to a yellow friable substance; so long as residual cores of elastic substance can be observed, the treatment with gas must be continued. The liquid is then poured off, and the nitrosite is washed with the solvent and roughly dried; it is then dissolved in acetone, and the filtered solution is concentrated. From this point onwards the procedure described on p. 404 may be followed. Ether is added to precipitate the nitrosite. Should there still be tarry matter or lampblack in suspension, a few cubic centimetres of ether are first added to precipitate these impurities without bringing down any nitrosite, and the solution is re-filtered and treated with excess of ether. The whole liquid, including the solvents and precipitate, is then evaporated, dried in a current of air or hydrogen, and weighed. Finally, the sulphur contained in the nitrosite is deter-

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[1] *Gummi-Zeit.*, 1907, **21**, 652; *J. Soc. Chem. Ind.*, 1907, **26**, 538.

mined. The whole of the chemically combined sulphur is stated by Alexander to remain in the nitrosite. The calculation to pure rubber is effected by the relation :—

$$2 \cdot 4 \text{ g. of sulphur-free nitrosite} = 1 \text{ g. of rubber.}$$

(b) *S. Axelrod's Tetrabromide Method.*[1]—1 g. of rubber is brought into solution by heating with 100 c.c. of petroleum of high boiling point. This will take two hours, or in some cases longer. Of the cooled liquid, which must be well shaken, 10 c.c., corresponding to 0·1 g. of material, are taken up in a pipette, and 50 c.c. of Budde's bromine solution (see p. 402) are added with constant agitation. After standing for three or four hours the mixture is diluted with 100-150 c.c. of 96 per cent. alcohol. The clear, supernatant liquid is poured off and the precipitate is rinsed on to a filter and washed first with alcohol and carbon tetrachloride in equal parts, and lastly with alcohol alone.

The white precipitate of tetrabromide includes the mineral filling materials of the rubber, and in addition contains a part of the sulphur of vulcanisation. The proportion of sulphur thus retained varies with the extent to which the rubber was vulcanised, but in no case amounts to the total sulphur of vulcanisation.[2] With soft rubbers it can be neglected without seriously affecting the determination of rubber; with rubbers of comparatively high vulcanisation it must be taken into account. In order to allow for the mineral matter, the weighed tetrabromide is incinerated with the addition of a drop or two of sulphuric acid, as in sugar analysis; by this means the errors introduced by carbonates and bromides are to a large extent counteracted. The net weight of tetrabromide finally obtained is multiplied by the factor 0·314 to give pure rubber.

GENERAL SCHEME OF ANALYSIS.

Special methods and individual determinations having been dealt with in detail above, the course of analysis of rubber goods as a whole may now be considered. The general principle followed is that, by means of solvents or of purely chemical operations, the various constituents are divided into groups, each of which receives further analytical treatment. A clear view of the scheme or schemes of analysis based on this principle is best given by means of Tables, four of which are appended.

Table I. illustrates an analytical procedure in accordance with the more recent developments of rubber chemistry. It is applicable to all classes of soft rubber goods, and also, except for the determination of inorganic fillers, to ebonites.

Gummi-Zeit., 1907, **21**, 1229; *J. Soc. Chem. Ind.,* 1907, **26**, 1058.
[2] W. A. Caspari, *Le Caoutchouc et la Guttapercha,* 1911, **8**, 5289.

Table I.

1. Extraction with Acetone (p. 425).				4. Determinations upon original material.
A. Extract:—	B. Separate portions of Residue.			
Free Sulphur.	2. Treatment with Alcoholic Potash (p. 425).		3. Treatment with Xylene under pressure, or Petroleum (p. 423).	Moisture.
Rubber Resins.	C. Extract:—	D. Residue:—	E. Solution:—	Ash (for qualitative examination).
Decomposed Rubber.	White Substitute (including Sulphur and Chlorine).	Vulcanised Rubber.	Vulcanised Rubber.	Total Sulphur.
Extract from substitutes.	Brown Substitute (including Sulphur).	Filling materials generally.	Substitutes.	Total Chlorine.
Extraneous Resins.	Blown Oils.		Extraneous Resins.	Antimony.
Rosin Oil.	Chlorine combined with Rubber.			Mercury.
Mineral Oil.	Small quantities of Zinc Oxide and Antimony Sulphide.		F. Residue:—	Sulphide-Sulphur.
Paraffin (Ceresin).	Extraneous Resins insoluble in Acetone, but saponifiable.		Filling materials generally.	Rubber by Axelrod's Tetrabromide method.
Fatty Oil.	(This residue may be used for Alexander's Nitrosite method.)			
Beeswax.				
Lanoline.				
Extract from Tars, Pitches, and Bitumens.				
Organic Dyes.				
Moisture.				

Table II.

Extraction with Acetone.

A. Extract:—

Free Sulphur.

Rubber Resins.

Extraneous Resins.

Rosin Oil.

Mineral Oil.

Paraffin (Ceresin).

Fatty Oil.

Extract from substitutes.

Beeswax.

Extract from Tars, Pitches, and Bitumens.

Lanoline.

Organic Dyes.

B. Residue treated with Alcoholic Potassium Hydroxide.

C. Extract:—

White Substitute (including Sulphur and Chlorine).

Brown Substitute (including Sulphur).

Blown Oils.

Chlorine combined with Rubber.

D. Residue:—

Vulcanised Rubber.

Filling materials generally.

In this residue are determined:—

Total Sulphur.

Ash.

Sulphur in the Ash.

Determinations upon original material.

Moisture.

Ash (for qualitative examination).

Total Sulphur, with quantitative analysis of Mineral matter.

Antimony and Mercury.

Carbonates.

Table III.

1. Extraction with Acetone.	2. Treatment with Pyridine (but see p. 426).	3. Treatment with Alcoholic Potash.	4. Treatment with Rubber Solvent.	5. Extraction with boiling water.	6. Determinations upon original material.
A. Extract:— Free Sulphur. Rubber Resins. Extraneous Resins. Rosin Oil. Mineral Oil. Paraffin (Ceresin). Beeswax. Lanoline. Fatty Oil. Extract from substitutes. Extract from Tars, Pitches, and Bitumens.	**B. Residue:—** **C. Extract:—** Bitumen. Tar and Pitch. Sulphur contained in the above.	**D. Residue:—** **E. Extract:—** White Substitute. Brown Substitute. Sulphur and Chlorine of substitutes. Blown Oils.	**F. Residue:—** **G. Extract:—** Vulcanised Rubber.	**H. Residue:—** **J. Extract:—** Starch. Dextrin. Flour. **K. Residue:—** Lampblack. Carbon from Pitch. Fibres. Mineral matter. (For quantitative analysis.)	Moisture. Ash (for qualitative examination). Total Sulphur, with determination of mineral matter. Antimony. Mercury. Carbonates. Sulphides.

Table IV.

1. Extraction with Acetone.

A. Extract:—

- Free Sulphur.
- Rubber Resins.
- Decomposed Rubber.
- Extract from substitutes.
- Extraneous Resins.
- Rosin Oil.
- Mineral Oil.
- Paraffin (Ceresin).
- Fatty Oil.
- Beeswax.
- Lanoline.
- Extract from Tars, Pitches, and Bitumens.
- Organic Dyes.
- Moisture.

B. Residue:—

2. Treatment with Epichlorhydrin.

C. Extract:—

- Resins insoluble in Acetone.
- Portions of the Tars, Pitches, and Bitumens.
- Sulphur combined with the above.

D. Residue:—

3. Treatment with Pyridine.

E. Extract:—

- Remainder of Pitchy matter.
- Sulphur, combined with same.

F. Residue:—

4. Treatment with Alcoholic Potash.

G. Extract:—

- Brown Substitute.

H. Residue:—

- Rubber proper, with Sulphur of vulcanisation.
- Filling materials.

In this residue are determined:—

- Total Sulphur.
- Ash.
- Sulphur in the Ash.

5. Determinations upon original material.

- Moisture.
- Ash (for qualitative examination).
- Total Sulphur, with determination of Mineral matter.
- Antimony.
- Mercury.
- Carbonates.
- Sulphides.

Table II. represents, with slight modifications, an older scheme for the analysis of comparatively simple materials, due to C. O. Weber.[1] It may be remarked that, according to the yet older scheme of Henriques, the first operation is extraction with alcoholic potassium hydroxide, followed by extraction with acetone. This method, though not now generally practised, has certain advantages in special cases, *e.g.*, for the separation of paraffin wax, mineral oils, and certain resins.

Table III. is an expansion of Table II.[2] and applies to the more complicated mixtures, such as goloshes, mechanicals, and goods of low quality.

Table IV. is that given by Weber[3] for the analysis of ebonites, with the addition of treatment with alcoholic potassium hydroxide to dissolve out substitutes. It is not often that substitutes as such are introduced into ebonites, but substances of this nature are very commonly produced in the ebonite in the course of vulcanisation. The inorganic filling materials cannot be isolated, as in the case of soft rubbers, but must be deduced from the composition of the ash and from the results of certain operations conducted on the ebonite itself.

Notes and Comments on the System of Analysis in Table I.

Group 1.—The mode of extraction with acetone, and treatment of the extract, have been described on p. 425. The residue must be completely dried before portions of it are weighed out for proceeding as under (2) and (3). The extract can in many cases be returned as "resin" or "acetone extract," any further analysis of it being dispensed with; as shown in column A, however, it may often be a very complicated mixture. The separation of the ingredients can be effected, with a moderate degree of accuracy, as follows :—

1. The extract is saponified and shaken out with petroleum spirit, according to the method described in the Section on "Lubricants," this Volume, p. 89; most of the free sulphur remains as sulphide in the alkaline solution. The petroleum spirit extract then contains mineral oil, paraffin wax, decomposed rubber, the unsaponifiable matter of resins, rosin oil, etc. These are dried and weighed in a flat porcelain dish, the bulk of the solvent having previously been distilled off. A few drops of concentrated sulphuric acid are then added, and the dish is heated for some time on a water-bath. The residue is mixed with a little fresh lime and animal charcoal, and extracted with petroleum spirit. There will now be in solution only

[1] *The Chemistry of India Rubber*, p. 256.   [2] *Loc. cit.*, p. 255.
[3] *Loc. cit.*, p. 258.

mineral oil, vaseline, paraffin wax, and ceresin, and this ·extract is again taken to dryness and weighed. A certain error due to loss of material must obviously be expected. From the appearance and consistency of the residue it will generally be possible to decide which of the above substances it consists of. If bitumen be present in the rubber, it may contribute a little paraffin to this residue. The difference between the total petroleum spirit extract and the purified residue represents matter which is not indifferent to sulphuric acid, *i.e.*, the un-saponifiable matter of rubber and other resins, the acetone extract of pitchy matter, etc. Any rosin (colophony) present in the rubber will go into solution in the alkaline liquid, on saponification. The soap-acids having been isolated, rosin is tested for by extracting with 60-70 per cent. alcohol, and submitting the extract to the Liebermann-Storch colour - reaction for rosin oil (see "Oils, Fats, and Waxes," p. 130).

2. An alternative procedure for splitting up the acetone extract is by means of alcohol. It is dealt with below (p. 438) in reference to cable insulations.

Group 2.—A portion of the residue B is taken for the quantitative determination of the substitutes, by the method described on page 425. So much of the substitute as is insoluble in acetone is thus obtained in solution, and its fatty acids can be isolated in the usual way. The fatty acids of pure substitutes are completely soluble in 90 per cent. alcohol at ordinary temperatures. They contain all, or nearly all, of the com-bined sulphur of the substitute, which may be determined in them by the nitrate-fusion method (see p. 419). This group further contains the chlorine of white substitutes, and a considerable proportion of the chlorine which is combined with rubber in cold-cured goods.

Residue D.—This contains all the rubber, all the sulphur of vulcan-isation, some of the chlorine of vulcanisation, and all of the solid fillers, except for what may have gone into solution (*e.g.* antimony) in alcoholic potassium hydroxide. If it be desired to carry out a rubber determina-tion by the nitrosite method, this is the material to use, because acetone-soluble matter and substitutes—especially the latter—are apt to prove a source of error in this method.

The remaining groups and operations call for no further explana-tion, all necessary observations being included on pp. 426-429.

INTERPRETATION AND STATEMENT OF ANALYTICAL RESULTS.

If a rubber analysis be conducted as described above, with the aim of reconstructing the original mixing, it will be found that few of the analytical results *per se* correspond directly to substances originally

forming part of the mixing. The reasons for this are—firstly, that analysis can divide up the rubber only into chemical groups, and not into raw materials; and, secondly, that rubber mixings of any great simplicity very seldom occur. Hence it may be regarded as sufficient to state the group results as such, which is what C. O. Weber recommended; or, if further knowledge be desired, the groups themselves must be subjected to further analysis. It is best, in the latter case, to resolve the analytical results into groups according to the scheme of Table I.

In this scheme it is especially column A and columns C and D of Group 2, which may call for laborious analytical subdivision; the analysis, however, is much facilitated by previous experience. It would be impossible to lay down general rules in small compass.

The subdivision of Group 3 is a comparatively straightforward matter. It should be noted that the amount of rubber hydrocarbon in the substance analysed is arrived at with a considerable degree of accuracy, by difference, according to Group 3; in a general way, this is quite as satisfactory as the direct determination of the rubber proper, if not more so. To find the amount of crude (washed) rubber originally incorporated, the rubber proper must be augmented by the rubber resin present. The latter is comprised in column A; to find its exact amount may or may not be a simple matter, according to circumstances.

The direct determinations enumerated in Group 4 may be of considerable value in elucidating the composition of a rubber. In regard to pitch and bitumen, it has already been stated that they are not amenable to a direct determination of any precision.

The following scheme of statement, in which all percentages are calculated upon the original material, may be found useful for analyses of rubber goods :—

1. Loss at 100° . . . . per cent.
2. Acetone extract . . . . per cent.
    Sulphur . . . ... per cent.
    Unsaponifiable matter . . ... per cent.
    Saponifiable matter . . ... per cent.
3. Substitute . . . . per cent.
    Sulphur . . . ... per cent.
    Chlorine . . . ... per cent.
4. Mineral matter . . . . per cent.
    The several constituents *seriatim* ... per cent.
5. Insoluble organic matter . . . . per cent.
6. Sulphur of vulcanisation . . . . per cent.
7. Rubber proper (by difference or by direct determination) ... per cent.
                                                    ——
                                                    100

THE EXAMINATION OF CABLE INSULATIONS, AND SPECIFICATIONS
FOR THE SAME.[1]

No generally accepted standards of a chemical character for the examination of rubber for cable insulations have been adopted in this country. In Germany, the official Prussian Institute for the Testing of Materials, in collaboration with a number of cable factories, has recently proposed a series of analytical standards, qualitative and quantitative, to be applied to the rubber coverings of standard electric cables. The specifications, together with the analytical operations involved, are as follows :—

Rubber for cable insulations is to be compounded thus :—

33·3 per cent. of rubber containing not more than 6 per cent. of resin.
66·7 per cent. of filling materials, including sulphur.

No organic filling material, except ceresin, or paraffin wax to a maximum amount of 3 per cent., may be incorporated.

The specific gravity of the vulcanised rubber is to be at least 1·5.

The material to which the above rules are intended to apply is the rubber insulation lying between wire and textile protection (tape, braiding, etc.) in its final condition, i.e., after undergoing any changes which vulcanisation in contact with impregnated fabrics may have wrought in it.

The laboratory examination is to extend to the following points :—

1. Determination of specific gravity.
2. Qualitative tests for mineral oil, bitumen, etc.
3. Determination of acetone extract, in which are to be determined :—
   a. Ceresin, or paraffin wax, and its content of sulphur.
   b. Total sulphur.
4. Determination of filling materials.
5. Determination of matter soluble in semi-normal alcoholic potassium hydroxide.

The insulation is to be rejected if it fails to come up to standard by any one of the above chemical tests. Should the specific gravity be less than 1·5, the chemical examination is to be proceeded with notwithstanding.

Methods of Analysis to be employed.

Preparation of the Sample.—Not less than 30 g. of rubber stripped from finished cables must be available for the tests. A length of cable

1 Cf. *Elektrotech. Zeitsch.*, 1909, **30**, 1205.

which will furnish at least this quantity must therefore be supplied in the first instance.

The rubber is comminuted by cutting into cubes of 0·5-1 mm. side with a pair of scissors.

1. *Specific Gravity.*—The material must sink in a zinc chloride solution having a specific gravity of 1·49 at 15°.

2. *Mineral Oil, Bitumen*, etc.—On allowing the material to swell in solvents such as xylene, carbon tetrachloride, pyridine, nitrobenzene, the solution must show neither fluorescence nor dark coloration.

3. *Extraction with Acetone.*—Two portions each of 5 g. are extracted with freshly distilled acetone for ten hours in a Soxhlet extractor, protected from sunlight. The two extracts, each in its flask, are freed from solvent by distillation and are dried to constant weight in an oven at 100°. One of the two extracts is dissolved by warming with 50 c.c. of absolute alcohol; the solution is filtered, washed with 25 c.c. of boiling absolute alcohol, and allowed to stand for an hour in a freezing mixture at −4° to −5°. The separated paraffin (with a little sulphur) is filtered off and washed with 100 c.c. of alcohol (90 per cent. by volume) similarly cooled. The filtrate is tested for paraffin by re-cooling.

The contents of the filter are washed by means of alcohol, followed by warm carbon bisulphide, into the original extraction-flask, where they are freed from solvent, dried at 100°, and weighed. This gives the whole of the paraffin plus a little sulphur.

To determine the sulphur in the above, about 20 c.c. of concentrated nitric acid (sp. gr. 1·48) are introduced into the flask and kept in gentle ebullition for half an hour; 100 c.c. of water are added, and the cooled solution is filtered. The filtrate is evaporated to dryness with a few crystals of sodium chloride on the water-bath, and then again evaporated with 5 c.c. of concentrated hydrochloric acid. The residue is finally dissolved in 50-100 c.c. of water, and precipitated with barium chloride as usual.

The contents of the second extraction flask are taken for the determination of the total sulphur in the acetone extract. The procedure is exactly as above.

Paraffin and sulphur being now known, the remainder on subtracting from the total acetone extract may be regarded as rubber resin.

4. *Filling Materials.*—A weight of acetone-extracted rubber (dried at 50°-60°) corresponding to 1 g. of original material is placed in a weighed 100 c.c. conical flask with 20 c.c. of petroleum, boiling point 230°-260° (or, if this fails, some other efficient solvent, *e.g.*, liquid paraffin or camphor oil), and heated under a reflux condenser until all the rubber is dissolved. The cooled flask is nearly filled with petroleum spirit, and the contents allowed to settle for twenty-four hours. A double-

bottomed Gooch crucible is prepared for filtration, dried, and weighed, and the decanted liquid is poured through again and again till clear; the sediment is then added, and the whole is washed with hot benzene until the filtrate is quite clear. After further washing with petroleum spirit, alcohol, and ether, both the crucible and the conical flask are dried at 105° and weighed.

In case a centrifugal machine is available, the filtration may be replaced by repeated whirlings and decantations with fresh petroleum spirit in the original flask; the latter is ultimately dried at 105° and weighed.

By the above operations the total pulverulent filling materials, including lampblack and fibre, are determined.

Filling materials, plus extracted sulphur, plus paraffin, taken together, must not exceed 65.7 per cent. The remainder counts as vulcanised rubber. To avoid the determination of the sulphur of vulcanisation, its amount is assumed by convention to be 1 per cent. upon the original material.

5. *Constituents Soluble in N/2 Alcoholic Potassium Hydroxide.*—After extraction with acetone, the rubber is dried at 50°-60°, transferred to a 100 c.c. conical flask, and boiled under a reflex condenser for four hours with 50 c.c. of a semi-normal alcoholic solution of potassium hydroxide upon a water-bath. The liquid is filtered and the residue is washed with 100 c.c. of hot absolute alcohol followed by 50 c.c. of hot water. The solution is evaporated to about 15 c.c., diluted with water to 100 c.c., and extracted with ether after acidification. The ethereal extract is cautiously evaporated in a tared beaker, dried to constant weight, and weighed.

As there is a certain small amount of matter soluble in alcoholic potassium hydroxide even in pure rubber, the allowable limit in cable insulations is taken as 0.5 per cent., calculated on the material itself.

MISCELLANEOUS NOTES ON THE ANALYSIS OF RUBBER AND OF RUBBER GOODS.

Coefficient of Vulcanisation is a term introduced by C. O. Weber to express the extent to which a rubber has been vulcanised. It is defined as the amount of rubber-combined sulphur per cent. of pure rubber (not per cent. of rubber plus combined sulphur).

Analysis of Proofed Fabrics.—In order to determine the proportion between rubber and fabric, the following method may be employed :—

An area of 50 sq. cm. is weighed and boiled with cymene, or the corresponding fraction of coal-tar naphtha. This solvent neither chars

the fabric nor decomposes any sizing which may be on it. When the rubber has gone into solution, the fabric is washed with cymene and then with alcohol, dried, and again weighed. It may then be further examined for sizing, etc.

To ascertain the composition of the rubber spreading, the proofed fabric may be dealt with as if it were solid rubber, by the ordinary methods of rubber analysis.

Rubber Solutions.—A great variety of solutions and cements containing rubber comes into trade for use in connection with tyres, waterproof goods, footwear, etc. The solid matter of such compounds is analysed in much the same way as ordinary manufactured rubber. To determine the total solids, a weighed quantity of the compound is dried in an oven to constant weight and re-weighed, the loss representing volatile solvent. This solvent will generally be carbon bisulphide, petroleum naphtha, or coal-tar hydrocarbons, or a mixture; in order to isolate and identify it, the method of R. Thal[1] may be followed. A weighed quantity is kneaded in a porcelain basin with several portions of 95 per cent. alcohol, which is poured into a measuring cylinder and copiously diluted with saturated brine. After a time the rubber solvents separate out as clear liquids; their volume is read off, and by taking the specific gravity their weight can also be determined. Boiling points and other characteristic properties serve to identify the solvents. Another simple way of separating solvents is to distil with steam; clear distillates which "break" readily without forming stable emulsions are thus obtained, but it is often difficult to drive off the last portions of solvent, except with an excessive amount of steam. Rubber solutions and cements are apt to contain foreign resins, gutta-percha, and balata.

Specific Gravity.—The determination of the specific gravity with rubber and rubber goods is carried out by the usual methods. It should be noted that rubber, even when finely divided, has a great tendency to enclose air; hence before weighing in a pyknometer, the sample must be well boiled out. The specific gravity of rubbers lighter than water is also best determined pyknometrically; even though the substance floats on the water, it can be taken in fragments large enough not to obstruct the capillary of the pyknometer.

A simple and easy way of determining the specific gravity is by flotation. The rubber is placed in a beaker of water, boiled out, and allowed to cool. Either alcohol or some indifferent salt (a saturated solution of zinc chloride may be used with advantage) is then added until solution and rubber have the same specific gravity; that of the former is finally determined by any convenient method.

An apparatus based on this principle for determining specific gravity has been devised by Minikes.[2] It takes the form of a test tube

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[1] *Chem. Zeit.*, 1898, 22, 737.　　　　[2] *Gummi-Zeit.*, 1898, 12, 97.

graduated in three sections; the middle third is marked on. the left side with divisions 2·00-1·45, counting upwards, whilst the upper third is marked on the 'right' side with divisions 1·50-1·00, counting downwards. · For comparatively light articles, water is poured in to the right-hand division 1·00, the sample introduced, and zinc chloride solution (sp. gr. 2·00) added little by little, with constant shaking, until the sample floats in the middle of the liquid; the specific gravity is then read off on the right-hand graduation. For heavier articles the tube is charged up to the lowest mark, viz. 2·00, with zinc chloride solution of sp. gr. 2·00, and water is added to equilibrium, the final reading being taken on the left-hand side.

Microscopic Examination.—This mode of examination has come more and more into vogue in recent times. The main obstacle has always been the difficulty of obtaining suitable micro-sections; a microtome is indispensable, and freezing and other stiffening devices have to be resorted to. It is now proposed to conduct the microscopic examination by the aid of reflected light, which greatly simplifies the examination. The thickness of the test-piece, under these conditions, is of no importance; all that is required is a smoothly cut upper surface. Microscopes specially adapted for work by reflected-light, with incandescent gas or electric illumination, are supplied by the makers, and are usually sent out with full directions for use.

D. EMPIRICAL TESTS APPLIED TO RUBBER GOODS.

There are numerous more or less cursory tests, both chemical and physical, to which rubber goods may with advantage be subjected by way of ascertaining whether they are likely to meet practical requirements. Such tests of course differ widely according to the class of material concerned: to realise this it is only necessary to consider a list of typical rubber articles, *e.g.*, elastic thread, dolls, balls, steampackings, insulations, hose - piping, ebonite combs, accumulator cells, etc. Whilst it would be impossible to enter into the more specialised tests, some of the more important and generally applicable tests are given below.

I. CHEMICAL TESTS.

1. **Dilute Acids.**—Specifications as to the resistance of rubber goods to the action of dilute acids are frequently laid down. They are especially significant in the case of packings and accumulator cells or grids.

(*a*) *Behaviour of Ebonite towards dilute Sulphuric Acid.*—The test may be applied to whole pieces or (less commonly) to comminuted material

as follows :—5 g. of plate or raspings are submerged in 25 c.c. of 20 per cent. sulphuric acid (sp. gr. 1·15), and kept at 50°-70° in a covered vessel for forty-eight hours. The ebonite is then washed well and dried at 95°-100°. The loss in weight should not exceed 4 per cent.

(b) *Resistance of Packings to Acid.*—A weighed ring or strip of material suitable for the tensile test by one or other of the testing machines referred to below (p. 445) is laid in 5 per cent. acetic acid, and left to itself for seventy-two hours at the ordinary temperature. It is then washed, dried, re-weighed, and subjected to the same tensile test as the untreated material. A second sample is warmed with the same acid to 60°-70° during forty hours, and dealt with similarly. The test is particularly valuable when its results can be compared with those given by material of known quality. Other acids than acetic may also be employed, in proper dilution.

2. Alkalis.[1]—The test is carried out precisely as that with acids. The alkaline solution may afterwards be evaporated to a small volume, acidified, and extracted with ether, the ethereal solution being then evaporated. The fatty acids, if any, thus obtained afford information as to oils or substitutes present in the rubber.

3. Alcoholic Alkali. — Extraction with alcoholic potash solution, without previous acetone extraction, is frequently laid down in specifications. Resin, free sulphur, and substitute are thus extracted together. The British Admiralty, which lays down a maximum loss of from 6 per cent. upwards, according to the nature of the article, prescribes "boiling for six hours in a finely-ground condition with a 6 per cent. solution of alcoholic caustic potash."

4. Saline Solutions.[2]—The material is subjected for a long time to the action of a 10 per cent. solution of the salt. Tests with sea-water also are sometimes prescribed.

5. Chlorine.[3]—A compact piece of material is weighed and laid in chlorine water ; the details of the test are the same as with acids.

6. Fatty and Mineral Oils.—A test-piece is immersed in oil and kept for seventy-two hours at the ordinary temperature, or for forty hours at 60°-70°. The gain in weight is then determined and comparative tensile tests are made. A specification sometimes laid down for cable insulations is that the gain in weight after four hours' treatment with oil at 70° shall not exceed 3 per cent. Beside gain in weight, increase of volume, which should also be as small as possible, may be observed, *e.g.,* by measuring the dimensions of test-pieces of rectangular contour.

7. Resistance to Oxidation.—See below under 8 and 10.

[1] From the chapter on Rubber, by E. Herbst, in Post's *Chemisch-Technische Analyse.*
[2] *Ibid.*   [3] *Ibid.*

II. PHYSICAL AND MECHANICAL TESTS.

8. Dry Heat Test.—The condition that rubber goods shall suffer no loss in suppleness or elasticity under the action of tolerably high temperatures is frequently insisted upon. The British Admiralty, for instance, specifies for " Mechanicals " that they shall " endure a dry heat-test of 270° F. (132° C.) for two hours without impairing their quality." According to Lobry de Bruyn,[1] the test is carried out by placing 3 g. of material, cut into thin sheet, in an oven previously brought to 135°, during two hours. After cooling, the rubber is compared with untreated material, from which it should not differ perceptibly.

9. Superheated Steam.—This, or a similar, test also occurs in Admiralty specifications. According to Lobry de Bruyn, a piece of the material is heated in a sealed tube, two-thirds filled with water, during four hours to 170°; the rubber should then have undergone no alteration.

10. Action of Light.[2]—A flat test-piece is fastened to a board, and one half of it is protected by a sheet of thick cardboard. It is exposed for a suitable period to direct sunlight. Rubbers sensitive to sunlight have a more or less marked tendency to develop superficial cracks and wrinkles under these conditions, owing to oxidation. The extent to which the rubber has suffered may be gauged by comparing the exposed with the unexposed half; over and above this, a standard rubber should be exposed concurrently.

The following oxidation test independent of sunlight has been proposed by Wolfenstein[3] and by C. O. Weber.[4] A sample is kept for two days in 20 g. of acetone mixed with 60 c.c. of hydrogen peroxide of 20 per cent. strength. After washing with a little acetone and water, and drying, the surface of the sample is inspected. The gain in weight, in comparison with a standard rubber, serves as a measure of the tendency to oxidation.

11. Permeability.—The capacity of sheet rubber or proofed fabric for retaining gases is of no small importance in aerial navigation. Qualitative tests may be made by stretching the material over a drum filled with hydrogen, coal-gas, air, or other gas under a slight plus pressure; the outer surface of the diaphragm having been painted with soap solution, it is easy to observe if and where there are pinholes. To make comparative quantitative tests, a drum covered and filled with gas as above is weighed when freshly charged, and again after twenty-four hours; from the change in buoyancy (assuming that a light gas,

[1] From Post, *Chemisch-technische Analyse,* loc. cit.   [2] *Ibid.*
[3] *Ber.,* 1895, **28,** 2665.   [4] *The Chemistry of India Rubber,* p. 230.

preferably hydrogen, is taken), the permeability per unit of area and per unit of time can be calculated.

12. Resistance to Pressure.—Compression tests may be, and currently are, carried out by a great variety of methods, mostly adapted to special circumstances. In the elaborate series of mechanical tests conducted by C. Heingerling and W. Pahl,[1] sheets of rubber of about 1 mm. thickness and 5 sq. cm. area were compressed for one minute under a maximum load of 4900 kg., and the resulting deformations were measured.

English railways prescribe compression tests for buffers, in which the buffer is subjected by means of a hydraulic press to loads of from 10-60 tons during specified periods; the deformation is measured immediately upon releasing the pressure, and at intervals afterwards.

13. Percussion Test.—A cube of about 1 cm. is subjected to the impact of a hammer-head of 2 kg. falling through 25 cm. The deformation undergone after, say, fifty blows have been delivered may be measured, or percussion may be continued until cracks appear in the rubber.

14. Insulation and Breakdown Voltage.—These highly important tests are very extensively applied to cable insulations and other rubber materials used in electrical engineering. They belong, not to the analyst's, but to the electrician's province, and for details concerning them treatises dealing with cables or electrotechnics generally should be consulted.

15. Resiliency.[2]—A solid or hollow ball of rubber is dropped from a given height on to a hard, even surface. Both the height of the first rebound and the time taken to come to rest may be measured, the results being compared with those given by a standard rubber.

By another form of resiliency test, a steel ball is dropped on to a thick plate of rubber and the rebound is measured.

16. Abrasion.—The general principle followed by machines designed for abrasion tests consists in pressing the test-piece under known loads against a rotating pulley or disc covered with emery-cloth or similar material; the abrasion undergone is compared with a standard. A special variety of this test is that applied to tyres by way of simulating road friction. In one patented machine the tyre is mounted on a wheel and pressed against a rotating drum, the surface of which is "paved" with rough concrete. The wheel is driven at high speed by means of a motor, and causes the drum to rotate with it. The test may be continued either for definite periods of time or until rupture of the tyre ensues.

17. Tensile Test.—This is on the whole the most valuable

[1] *Verh. Ver. Bef. Gewerbfl.*, 1891, p. 370.
[2] From Post, *Chemisch-technische Analyse*, loc. cit.

mechanical test for defining the quality of a rubber. It is less empirical, and represents a closer approach to fundamental reliability, than any of the tests enumerated above, and its results can be expressed with considerable quantitative precision. It must be understood, however, that the science of the mechanical properties of rubber is as yet in a very inchoate condition, not being nearly so far advanced as that of the testing of metals, incomplete as that is. Results of tests are affected very extensively according to laws which are not yet cleared up, by the size and shape of the test-piece, the method of clamping, the rate of extension, and other factors. Hence, on the one hand, comparable and consistent quantitative data can only be obtained by using one definite kind of machine and test-piece, and by carrying out the test with rigorous uniformity. On the other hand, no generally accepted conventions have been arrived at by which one specified method, as in cement-testing, is adopted as standard. With these reservations, the fact remains that comparative tensile tests are a very serviceable means of differentiating one rubber from another, so far as mechanical properties are concerned.

The principal quantitative data afforded by the tensile test are:—
(1) breaking stress (usually expressed in kilograms per square centimetre), (2) elongation at rupture (expressed as a percentage), and (3) modulus of elasticity (Young's modulus). The latter is not a constant quantity within limits, as in the case of steel, but must be stated with respect to a given stress or elongation.

Numerous forms of testing machine have from time to time been designed, and some of them have become current articles of commerce. Within the limits imposed by the size, scope, and elaboration of the machine, all those named below are capable of giving useful comparative results. The two first are large, workmanlike constructions, and can deal with loads of 100 kg. or over.

L. Schopper's [1] *Machine* is of the upright type, the power being applied hydraulically, and stresses being measured by means of a pendulum-lever working over a sextant (Fig. 56). This design, which has long been in use in connection with the testing of paper and fabrics, has been adapted to the exigencies of rubber largely by the aid of the Royal Prussian Testing Institution. The test-pieces take the shape of rings, which are stamped out of thick sheet with a specially constructed press (Fig. 57); they are gripped by rollers, one of which is kept in continuous rotation during the extension, whereby the ring also is made to change its points of support continuously.

P. Breuil's [2] *Machine* (Fig. 58) is a strong horizontal apparatus

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[1] *Cf.* Frank, *Gummi-Zeit.*, 1908, **22**, 6; Schidrowitz, *India-Rubber Journal*, March to May, 1909; Memmler and Schob, *Mitt. k. Materialprüf.*, 1909, p. 4.
[2] *Le Caoutchouc et la Guttapercha*, 1907, **4**, 1061.

working with flat test-pieces held in grips of the ordinary vice pattern; power is applied by hand through a long screw and bevel-gear, and stresses are read off on the dial of a spring balance. By the aid of auxiliary appliances, the machine may also be used for tests by compression, by alternating stress, by abrasion, and at high or low temperatures.
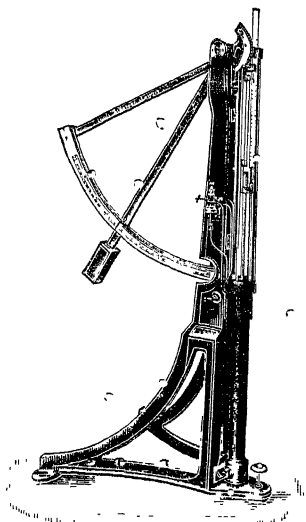
FIG. 56.
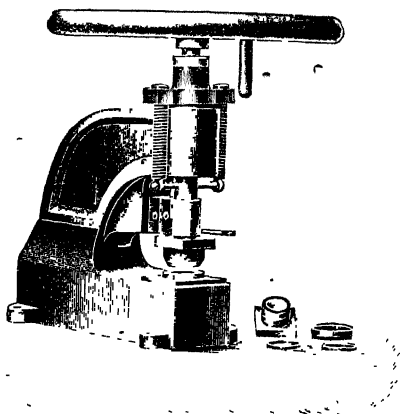
FIG. 57.

L. Delaloe's Machine is a small portable apparatus which was in use for leather, fabrics, etc., before it was applied to rubber testing. The mechanical principle is the same as that of Breuil's machine.
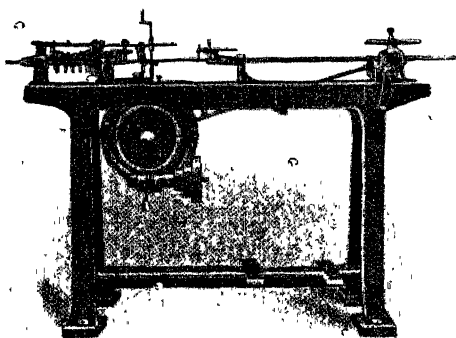
FIG. 58.

A. Schwartz' [1] *Machine* embodies a new departure, in that it is arranged to determine, not the breaking strength of the rubber, but its behaviour under intermediate strains and stresses. It takes flat test-pieces of slender dimensions; stresses and elongations are not directly read off, but are continuously recorded graphically. Emphasis is more especially laid on the "hysteresis-loops," registered on the diagram when a test-piece is stretched to a point short of rupture, and then allowed to contract by virtue of its own elasticity.

[1] *J. Inst. Elec. Eng.*, 1910, 44, 693.

Schopper's and Breuil's Machines are also fitted with accessory gear, enabling stress-strain diagrams and hysteresis-loops to be automatically recorded.

C. Beadle and H. P. Stevens' [1] *Machine* measures the breaking strength and elongation of ring-shaped test-pieces which are not rotated. The test-rings are punched out of sheet as with the Schopper machine, but are lighter and flatter. The disposition of the machine is horizontal; power is applied by water run from a tap into a suspended bucket, and stresses are measured by weighing the bucket and its contents.

18. **Bending Stress.**—For ebonite, the tensile strength of which is not so interesting as that of soft rubber, the most useful test is that by bending. A bar or rod of ebonite is firmly clamped at one end in a horizontal position, and weights are applied at the other end until rupture ensues. The load and the angular displacement at rupture are measured.

By the recently adopted specifications of the British Admiralty,[2] the rod is not bent to rupture, but is loaded with a specified weight and exposed to a temperature of 70° C. during two hours. At the end of this time the point of support of the weight must not have sagged more than a specified distance.

19. **Washers for Bottle-stoppers** may be subjected to the following comparative test:—The washers are slipped on to stoppers of the proper size, when they will be under slight strain, and exposed for five days to direct, or for ten days to diffused sunlight. If after this time a washer shows any cracks, wrinkles, indentation, or incipient stickiness, it may be regarded as unfit for use.

GUTTA-PERCHA AND BALATA.

(a) Gutta-percha.

1. Gutta-percha is a gum which resembles india-rubber chemically, but differs from it in mechanical consistency. It is coagulated from the latex of a series of trees belonging to the family of *Sapotaceæ*. The old-established method of collecting gutta-percha involves the preliminary felling of the tree; latterly, however, much attention has been given to replacing this ruinous procedure by methods of "milking" the living tree. Gutta-percha trees are limited in their habitat to the Malay Peninsula, Sumatra, Borneo, and the Philippines. In recent times plants yielding gutta-percha have been discovered in the Soudan and in German New Guinea.

Beside that which is derived from latex, a certain amount of gutta-

[1] *J. Soc. Chem. Ind.*, 1908, **28**, 1111.   [2] *India-Rubber Journal*, 1913, **45**, 1192.

percha comes into the market which is obtained from leaves and twigs, either by extraction or by mechanical processes. This mode of production has been more especially developed in the Dutch colonies.

The main points of difference between gutta-percha and india-rubber are the following:—When heated to temperatures below 70°, gutta-percha becomes soft and plastic like wax. The cooled mass retains any shape that may have been impressed on it. The elasticity of gutta-percha is inconsiderable, and not to be compared with that of rubber. On the other hand, gutta-percha has a much higher insulation resistance than unvulcanised rubber.

The characteristic constituent of gutta-percha is a hydrocarbon, to which the distinctive name "gutta" is sometimes applied. It is a polymerised dimethyl-*cyclo*-octadiene $(C_{10}H_{16})_x$, isomeric with caoutchouc. Whilst in its purely chemical relations gutta comports itself almost exactly like caoutchouc, it differs notably in its behaviour towards solvents.[1] Gutta solutions are far less viscid than rubber solutions, and, unlike the latter, deposit pseudo-crystalline flakes on cooling, which retain much solvent, but show no tendency to coalesce. Again, gutta dissolves much less readily in ether than caoutchouc; hence gutta solutions can usually be precipitated by means of ether, which is not the case with rubber solutions.

Gutta-percha resin has been an object of investigation from early times, and has been empirically divided into two constituents, *Albane* and *Fluavil*. It appears from the work of P. van Romburgh[2] that gutta-percha resin consists, at any rate to a large extent, of esters which on saponification yield cinnamic acid, and alcohols resembling cholesterol.

Crude gutta-percha, as imported, contains moisture, dirt, gutta proper, and oxygenated substances grouped under the heading of resin. To render it fit for use industrially, it is washed like rubber between rollers or in kneading machines. A further process of purification, so-called "hardening," often applied to gutta-percha, consists in removing the bulk of the resins by means of solvents.

2. *The Examination of Gutta-percha.*—This comprises the following determinations:—

(1) Moisture.
(2) Ash.
(3) Mechanical impurities.
(4) Resin.
(5) Softening point.
(6) Electrical and mechanical tests.

(1) and (2), *Moisture and Ash*, are determined as in the case of rubber.

[1] *Cf.* W. A. Caspari, *J. Soc. Chem. Ind.*, 1905, 24, 1274.   [2] *Ber.*, 1904, 37, 3440.

(3) *Determination of "Dirt."*—Owing to the difficulty of sampling ordinary crude gutta-percha, there is not much to be gained by going beyond the determination of mechanical impurities plus moisture in the washing process. In order to determine dirt in washed or unwashed gutta-percha on the laboratory scale, about 1 g. of material is dissolved in chloroform, toluene, or the like; the insoluble residue is collected on a tared glass-wool filter, washed, dried, and weighed.

(4) *Determination of Resin.*—The most important analytical datum with regard to a gutta-percha is its resin-content, the determination of which should never be omitted. The resin-contents—which vary within wide limits—of many sorts of gutta-percha have been given by E. Obach.[1] To determine resin, the simplest method would be direct extraction, as described for rubber under A (p. 400); but gutta-percha does not lend itself well to this procedure, because by the melting of the superficial layers access of solvent to the interior is rendered difficult or impossible. The following method may be recommended[2]:—A gutta-percha solution as obtained after the dirt has been separated (see above), or an aliquot part of the same, is concentrated to a volume of 10-15 c.c. and poured, whilst still warm, into 75 c.c. of boiling acetone. The flask is rinsed with a little of the same solvent. The mixture, from which the gutta will have been instantly coagulated, is boiled for ten minutes under a reflux condenser in order to redissolve any coprecipitated resin. The clear liquid, containing all the resin, can then be poured off; the firm coagulum of gutta hydrocarbon, on the other hand, can be transferred to a tared glass-wool filter, washed, dried, and weighed.

According to the method of Tromp de Haas, a gutta-percha solution is evaporated in a wide-mouthed flask or conical beaker, so as to yield a thin uniform film. The latter is repeatedly boiled out with acetone, and the residual gutta hydrocarbon is dried and weighed without transference.

A simple method for the determination of resin, which makes no pretensions, however, to the highest accuracy, is described by E. Obach. The principle consists in treating a weighed quantity of gutta-percha with a definite volume of resin-solvent and eventually determining the density of the solution so obtained. Obach's apparatus consists of two upright stoppered cylinders communicating with one another by narrower tubes. One cylinder is charged with gutta-percha, the other with a measured volume of ether. The latter is driven by air-compression into contact with the gutta-percha, on which it is allowed to act for some time. The solution is then sent back into the empty cylinder, which contains a hydrometer and a thermometer, and its density is

[1] Cantor Lectures on Gutta-percha, *J. Soc. Arts*, 1898.
[2] Frank and Marckwald, *Z. angew. Chem.*, 1902, 15, 40.

directly·read off. In order to prevent loss of ether by evaporation, the apparatus is mounted in a wooden box having panes of glass at the front and back. Tables have been drawn up giving the relation between the density of the solution and the percentage of resin in the gutta-percha.

To determine the dirt and resin in gutta-percha, van Romburgh proceeds as follows :—1 g. of material is placed into a 100-c.c. measuring flask with 80 c.c. of chloroform and heated for an hour on the water-bath, with occasional shaking. When the whole has dissolved, the solution is cooled and made up to 100 c.c. It is then filtered through cotton or glass wool (previously extracted), packed in a funnel, the stem of which should be about 20 cm. long, with a 3 mm. bore; the filtration should be carried out expeditiously. The first 50 c.c. of clear filtrate are poured into a weighed wide-mouthed conical-flask of about 200 c.c. capacity. The solvent is distilled off in such a way as to leave a uniform film of substance; this is dried, whilst standing in hot water, by a current of carbon dioxide, allowed to cool, and weighed. The result multiplied by two gives the weight of soluble matter, which, subtracted from the original material, gives the mechanical impurities plus moisture. The contents of the flask are next boiled out with three relays of acetone. In boiling, and in pouring off the acetone, care must be taken not to let the substance run together into a compact lump. The residue is redissolved in chloroform and again evaporated to a film, and is then again exhausted with boiling acetone. Finally, it is dried in carbon dioxide and weighed. This gives the gutta proper, which is to be multiplied by two as before.

(5) *The Softening Point.*—The following method is given by E. Obach. Similarly shaped strips of the gutta-perchas to be compared, or of manu-factured articles, are fastened to a frame, upon which they are held taut by means of springs. The frame is immersed in a water-bath, which is gradually heated up, and the apparatus is so arranged that an electric bell is rung when each strip, by becoming soft, releases the spring to which it is attached. When this takes place, the temperature of the water is read. The time taken by a softened test-piece to regain its hardness may also be determined.

(6) *Other Physical and Technical Tests* are adapted as far as possible to the conditions under which the material is to be used in practice. In general, the methods are much the same as for rubber. Electrical properties, such as insulation resistance, specific inductive capacity, and breakdown voltage, are of especial importance in the case of gutta-percha, and call for careful measurement. Different sorts of gutta-percha vary to a surprising extent in these respects. For details, the monograph of Obach, referred to above, may be consulted.

(*b*) Balata.

Balata is a substance very similar to gutta-percha. It is prepared by coagulating the latex of certain trees belonging equally to the group of *Sapotaceæ*, notably *Mimusops Balata* or *Sapota Mulleri*. The chief occurrences of *Mimusops* are in Jamaica, Trinidad, Venezuela, Guiana, and the Amazon valley; also to a minor extent in Africa.

The valuable constituent of balata is a hydrocarbon resembling gutta-percha; it is associated with a rather large proportion of resin.

The laboratory methods applicable to balata are precisely the same as for gutta-percha. Unmixed balata is not employed for insulations, owing to its comparatively low softening point. Balata is used in large quantities in the manufacture of belting. It is also added to rubber mixings which are required to vulcanise slowly, or in order to impart increased resistance to wear to the vulcanised goods.

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VEGETABLE TANNING MATERIALS

By the late Prof. C. COUNCLER, Ph.D., formerly Professor of Chemistry in the Royal School of Forestry, Munden. English translation revised by Prof. H. R. PROCTER, M.Sc., late Director of the Leather Industries Laboratories, The University, Leeds.

Preliminary Notes on the Estimation of Tannin.

In the quantitative estimation of tannin, peculiar difficulties have to be overcome. The majority of tanning substances are not yet sufficiently well known to permit of their being separated and weighed either in the free condition or in the form of characteristic compounds. However, as commerce has demanded a quantitative determination of " tanning value," numerous methods for the estimation of tannin have been devised. None of them satisfy the claims of exact science, but results which are adequate for practical purposes can be obtained if " tannin " be defined as " that which tans," *i.e.*, those organic substances which are absorbed by hide from solution and which increase its dry weight. In the majority of cases several different chemical compounds are present, which are estimated under the general name of " Tannin " or " Tanning substances." The Research Stations have, until now, carried out the quantitative analysis either with the Loewenthal method (improved by von Schroeder) or by means of a gravimetric method. The tannin is brought into solution, and either of the following determinations is made before and after the removal of the tannin by means of hide powder :—

A. The permanganate value in the cold (Loewenthal); or

B. The dry content (gravimetric methods) of a small quantity of the solution. In both cases the tannin is calculated from the difference.

Finally, the tannin content may be gauged roughly by ascertaining the specific gravity in the cold of a portion of the aqueous solution (hydrometer method); this process gives uncertain results, but possesses a certain practical value.

It must also be noted that two chemists, using any one of these methods, can only obtain concordant results if they work to the same prescribed conditions. In 1883 most of the laboratories interested

accepted a standard method of using the Loewenthal method, which is frequently followed at the present day. A general gravimetric method, which has been accepted by leather trades chemists, has been laid down by the International Association of Leather Trades Chemists (I.A.L.T.C.), first in 1897 in London, then in 1898 at Freiberg, which also includes the estimation of moisture, and which is appended to this Section.[1]

All such uniform methods working to pattern are empirical, and will in course of time be improved; the subjoined descriptions are necessarily restricted to their present condition.

Hide Powder.

As a means of precipitation hide powder is of undoubted utility in the best methods of tannin analysis. Even the Loewenthal-von Schroeder method utilises the best possible hide powder; to a much greater degree must this be the case with gravimetric processes. Hide powder of the prescribed quality can be obtained from the German Leather Industries Research Institute at Freiberg (Saxony).

The gravimetric method described in the fourth German edition of this work, with which von Schroeder and the author obtained concordant figures, cannot be generally adopted, as it demands too great purity of the hide powder. Nowadays freshly chromed hide powder, the preparation and chroming of which will be described later (p. 472), is used both in the standard gravimetric method and in Procter and Hirst's modification of the Loewenthal process. Unchromed hide powder precipitates less "reducing non-tans" than the chromed variety, giving therefore more scientifically correct results; yet the chromed hide powder gives far more concordant results between different analysts, while the gravimetric method only determines a small proportion of the permanganate reducing non-tans.

A. NON-GRAVIMETRIC METHODS OF TANNIN ANALYSIS.

I. THE LOEWENTHAL METHOD, IMPROVED BY VON SCHROEDER.

Principle.—The aqueous solution of the tannin is oxidised with a permanganate solution of known activity, and from the amount of permanganate solution required the amount of tannin is calculated. Since the tannin solution generally also contains reducing substances which are not tannins, the permanganate value (a) of the original solution is first obtained, and then (b) that of a similar volume of

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[1] *Cf.* H. R. Procter and H. G. Bennett, "The Present Development of the Analysis of Tanning Materials," *J. Soc. Chem. Ind.,* 1906, **25,** 1203 ; 1907, **26,** 79.

solution which has been detannised by means of hide powder. The difference (a-b) gives the permanganate value corresponding to the original tannin present.

Reagents Required.

1. *Permanganate Solution.* — 10 g. of the purest potassium permanganate are dissolved in 6 litres of distilled water.

2. *Indigo Solution.* — 30 g. of solid sodium sulphindigotate are brought in the air-dry condition into 3 litres of dilute sulphuric acid (1 : 5 by volume), 3 litres of distilled water are added and thoroughly shaken up until complete solution is obtained; then the whole is filtered. In every titration 20 c.c. of this indigo solution are diluted with $\frac{3}{4}$ of a litre of water; this will then reduce about 10·7 c.c. of the permanganate solution.

3. *Hide Powder.*—Must be thoroughly white and quite woolly, and must contain no materials extractable with cold water, which would reduce permanganate solution. To make absolutely certain, it is customary to do a blank experiment with 3 g. of hide powder.

4. *The Purest Tannin.* (See the Interpretation of the Titration, p. 455.)

The Method of Titration.

To the $\frac{3}{4}$ litre of solution containing the indigo solution and tannin, the permanganate is added from a stoppered Geissler burette.

(*a*) **Drop Method.**—According to Neubauer, the tap of the burette is so turned that the permanganate solution drops slowly (1 drop per second) into the solution under titration; whilst the addition is proceeding the solution is vigorously stirred with a glass rod, until a bright green colour is obtained. Then the tap is turned off and the permanganate slowly added in single drops at considerable intervals, and well stirred, and the procedure continued until the solution loses its last trace of green and becomes pure yellow.

(*b*) **The One Cubic Centimetre Method.** — According to von Schroeder, 1 c.c. of permanganate solution should be added at a time, and the solution stirred vigorously for five to ten seconds. When the solution has become light green in colour, only 2-3 drops are added at a time, and this procedure continued until the liquid appears a pure golden yellow.

The thick-walled beaker which contains the solution to be titrated is placed on a white porcelain tile, in order that the end-point of the reaction may be easily observed.

Over-titration should be strictly avoided, as titrating back is quite

impossible. In the carrying out of a tannin estimation, as good an agreement must be obtained as in ordinary titrations.

The permanganate value is a function of several variables; it is especially dependent on the time, *i.e.* the rate at which the permanganate is added to the indigo, and the rapidity of stirring.

If the "drop method" has been used to standardise a permanganate solution, the same method must be used in performing an analysis with that solution, using the figure thus obtained.

Interpretation of the Titer of the Permanganate Solution.

The purest possible commercial tannin is standardised in the following manner:—2 g., air-dried, are dissolved in 1 litre of distilled water, and the permanganate value of 10 c.c. of this solution (with the addition of indigo solution, whose reducing power is known, see above) is obtained.

As *pure* gallotannic acid cannot be obtained, Procter and Hirst[1] recommend the use of pure crystallised gallic acid, and have determined its value as compared with that of the gravimetric method for most commercial tanning materials (see p. 459).

Further, the permanganate value after detannisation with hide powder is obtained, 50 c.c. of tannin solution being used. This 50 c.c. is placed in a tightly closed glass bottle with a glass stopper for eighteen to twenty hours with 3 g. of hide powder, which has been first soaked and then well squeezed out, shaking frequently; it is then filtered and 10 c.c. of the supernatant solution again titrated.

The permanganate value of the hide powder filtrate should not be more than 10 per cent. of the total permanganate required. By drying at 100° to constant weight, the moisture content can be estimated, from which the total permanganate value (see p. 461) of the dry matter of the tannin is calculated; the result so obtained, multiplied by 1·05, gives the true titration value.

The reason for calculating the titration value to tannin instead of to oxalic acid, etc., is that by this means the same effect due to the rate of addition of the permanganate solution is obtained as with the unknown tannin, which would not be the case with oxalic acid, oxalates, ferrous sulphate, etc.

The Method of Tannin Analysis.

1. Preparation of the Tannin Solution.

(*a*) Extracts are dissolved in hot water, and filtered if required.

(*b*) Raw Tanning Materials (Barks, Fruits, Woods, etc.).—The tannin is efficiently extracted by means of the Tharandt extraction

[1] *Collegium*, 1909, p. 187.

apparatus (see below).   The extracted liquor after cooling is made up to 1 litre at room temperature, and if not absolutely clear, an aliquot part is filtered.

The following quantities are used for an analysis :—

	Per cent.
20 g. tanning material if containing probably . . .	5-10
10 g. tanning material if containing probably . .	10-20

5 g. tanning material if containing higher percentage.

The materials richer in tannin (quebracho extract with 66 per cent. and higher content, etc.) can be taken in smaller quantities, e.g. 3 g.

The sampling of tanning materials is somewhat difficult.   The best samples can be drawn from the well-ground and mixed material. With bad sampling from the same parcel of oak-bark samples of 5 per cent. and 10 per cent. tannin content can be obtained.   Of the many publications on the most efficient means of sampling those of F. Kathreiner are especially important (see p. 464 under C).

2. Titration of the Tannin Solution.

The tannin content of an aqueous solution is estimated by the Loewenthal-von Schroeder method by titration of 10 c.c. of solution (see p. 453) before and after treatment with hide powder (3 g. to 50 c.c. solution, as in interpretation of the titration).

The content of the tannin solution must be such that 10 c.c. of the same reduce 4-10 c.c. of permanganate solution (neither more nor less, as the tannin content is not absolutely proportional to the permanganate value).

Extraction Apparatus.

Of the many forms of extraction apparatus that have been proposed the Tharandt apparatus (bottle extractor) of von Schroeder and R. Koch (Fig. 59) is one of the best.   This consists of a wide-mouth thick-walled 200 c.c. glass bottle, B, into which a layer of sea-sand is poured to a depth of 1 inch, the latter having been previously thoroughly extracted with hot hydrochloric acid and water, and then well dried.   The tanning material G to be extracted, already soaked in water, is placed in the bottle B with more water, and the whole closed with a tightly fitting double-bored rubber stopper.

Through one hole in the stopper passes a glass tube, H, bent twice at right angles, with one end cut off sharply just below the stopper. Through the other hole a similarly bent tube is passed, which reaches

right down to the bottom of the extraction vessel B, becoming wider at the bottom (F). This latter tube is best made from a thistle funnel, such as is used in the production of gases; this is passed through the hole in the stopper and then bent at right angles. The thistle top F has a projecting curved edge, and is closed with a double layer of gauze, so that while fluids can pass through from B to F, solid bodies cannot. The lower end of F reaches into the sand. The extraction apparatus, filled and closed with the rubber stopper carrying the tube H and the funnel F, is placed upon the filter paper in the water-bath E, which is supported by a tripod, E, and the stopper pushed tightly home. The tube H is also filled with water, and connected by *b* through a rubber tube to the pressure tube J, which is filled with water from the reservoir A, the latter containing at least 2 litres. *a* and *b* are each fitted with a double screw cock to regulate or stop the flow
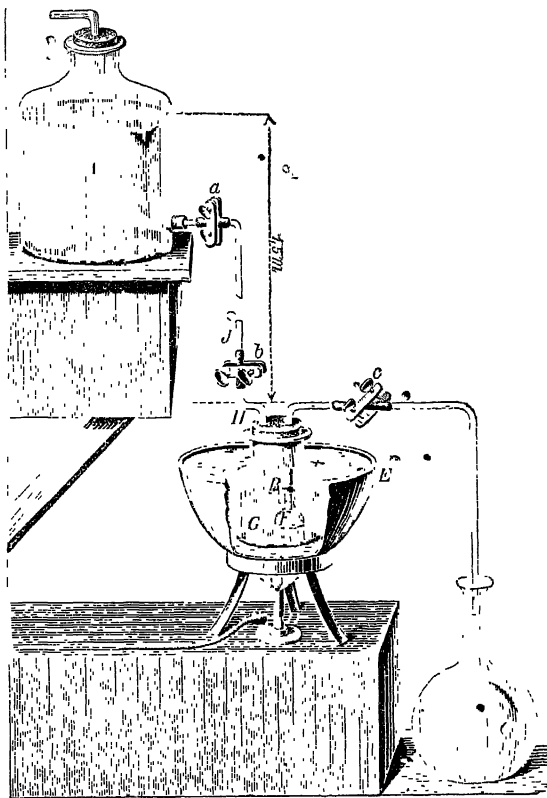
FIG. 59

of water when required, though experts can dispense with the cock *a*. The fall of water should be about 5 feet. The rubber tube at *e* is also fitted with a double screw cock, which is now closed, and the right angle delivery tube passed into the litre flask C.

This apparatus is suitable for the special estimation of easily and difficultly soluble tans, without its being necessary to transfer the material to any other apparatus. After the material has been subjected to the water pressure for fifteen hours by opening the cocks at *a* and *b*, while *c* is closed, it is only necessary to open the cock at *c* and regulate the flow, to fill the litre vessel C to the mark in three hours. This then contains the easily soluble tannin. The flow from *c* is then stopped and a fresh litre flask placed in position, the water-bath

heated to boiling by the flame D, and the difficultly soluble tannins extracted.

If it be required to estimate the total tannin, the water-bath E is heated from the beginning of the extraction. The first 500 c.c. are extracted below 50°, after which the temperature is rapidly raised to boiling point. The Loewenthal method, as described, can be used on solutions to solve many important commercial problems, and has rightly been widely adopted.

Unfortunately, Loewenthal results are frequently confounded with the gravimetric results. If the analysis of a pine bark gives 10 per cent. of tannin by the Loewenthal method, this means that the tannin extracted from this pine bark reduces as much permanganate (under prescribed conditions) as if it contained 10 per cent. of tannin. Nevertheless, the material may contain 17 per cent. gravimetrically, as it has long been known that it was quite impossible to compare, for example, sumac and pine bark by the Loewenthal process. It has been thought that different samples of the same material might be compared by means of the Loewenthal figures, but researches at the Vienna Research Station[1] have shown that even this view is fallacious. In addition, the results of the Loewenthal and gravimetric methods bear no constant relationship to one another, indeed the differences between oak and pine vary greatly. The same facts have been adduced by Zeumer.[2]

II. H. R. PROCTER AND S. HIRST'S MODIFICATION OF THE LOEWENTHAL METHOD.[3]

This process has been largely adopted since it has been shown that the comparison of the results of the Loewenthal and gravimetric methods provides a good means of detecting the adulteration of tanning extracts with sulphite cellulose liquors. Concentrated sulphite cellulose liquor — often wrongly called "Fichtenholzextrakt" — only gives extremely low percentages of tannin by the Loewenthal method, whilst, as it contains a large quantity of substances absorbable by hide, the results by the gravimetric method may be high.

Only a few small changes have been introduced to simplify the process. Self-filling burettes are used for the permanganate and indigo solutions (see Fig. 60), and the titration is carried out in a large glass jar of about 1 litre capacity, in which a small double-vaned stirrer, turned by a water turbine or a motor, is suspended. For purposes of comparison a similar beaker, containing a similar solution previously

[1] *Gerber*, 1887, p. 2.　　[2] *Tharander forstliches Jahrbuch*, 1886, **36**, 141.
[3] *J. Soc. Chem. Ind.*, 1909, **28**, 294.

titrated to the colour required, is placed alongside as a standard. The titration can thus be carried out rapidly with absolutely concordant results, and this method may be strongly recommended for the systematic control of tannery liquors. As tanning materials are now almost always bought and sold on the analysis by the Standard International method, and as this involves the removal of the tannin with chromed hide powder, the latter process is also to be recommended for use in this modification of the Loewenthal method. Formerly the Loewenthal figures were always calculated on pure gallotannic acid, for which Procter substitutes pure recrystallised gallic acid, which is easy to obtain, which is oxidised in the same way as tannin, and 1 g. of which reduces the same amount of permanganate as 1·34 g. of the purest gallotannic acid.
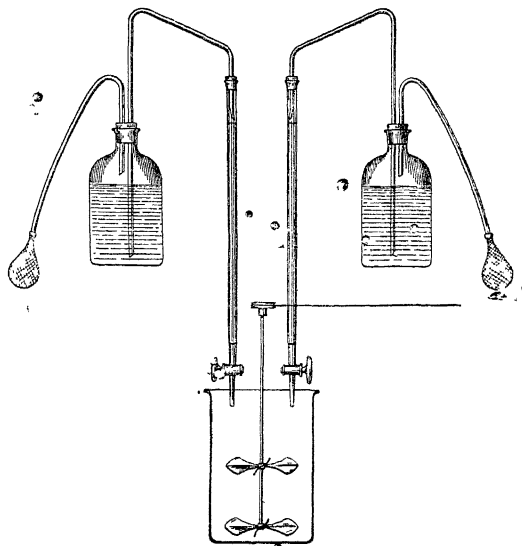
FIG. 60.

Solutions Required.

1. Pure air-dried gallic acid, 0·1 g. freshly dissolved in 100 c.c. of water.

2. Purest indigo carmine, 5 g. per litre, plus 50 g. concentrated sulphuric acid; 25 c.c. indigo solution are taken for every titration. 1 g. "indigo pure," B.A.S.F., dissolved in 25 c.c. concentrated sulphuric acid, diluted to 1 litre, and mixed with another 25 c.c. of sulphuric acid, can also be used. These two solutions keep well; 25 c.c. of either are oxidised by 25-30 c.c. of permanganate, in default of which a larger or smaller quantity of indigo solution must be taken.

3. Permanganate solution, 0·5 g. per litre. This is prepared by the suitable dilution of a 5·0 g. per litre solution immediately before use, as very dilute solutions do not keep well.

The Method of Titration.

The tannin solution (liquor) must be so diluted that 5 c.c. of the same do not reduce more than two-thirds of the quantity of

permanganate reduced by the original 25 c.c. of indigo solution; the contents of a 50 c.c. burette are therefore sufficient for a complete titration.   The stirring must be uniform, the addition of permanganate also uniform and at such a rate that the drops can be counted, until the colour of the solution becomes yellowish-green.   The permanganate is then slowly added, drop by drop, until the pure yellow colour is obtained.   To ensure uniformity of work, the titration should be carried out in a fixed time.   The titration is effected more easily by good artificial light behind matt glass than by daylight, as the disappearance of the last trace of green is more accurately observed; but every analysis must be carried out under the same rigid conditions, as otherwise the end-point can not be uniform.   (See p. 472, Standard Gravimetric Method; section 7, "Detannisation.")

Tanning matter is calculated from the difference between the permanganate required for the original and for the detannised liquor; as dissolved salts and traces of hide substance have no appreciable influence on the titration, the detannisation can be carried out more easily than in the gravimetric method.   The hide powder is only chromed, squeezed, weighed, and the necessary water added (see p. 472), the washing of the powder after chroming being unnecessary; and when 20 g. of water have been added with the hide powder to a 100 c.c. solution, 6 c.c. of the detannised solution are calculated as 5 c.c.

Still simpler in use are Paessler's "weakly chromed" hide powder,[1] or Kopecky's freshly air-dried shavings of chrome leather.[2]   About 7 g. of the dry hide powder and some kaolin are added to 100 c.c. of the diluted liquor, well mixed by hand-shaking, and then shaken for ten to fifteen minutes in a machine.   The moisture content of such a quantity of hide powder is at the most 1 g., and can only produce a maximum error of 1 per cent. of the total tannin in the diluted solution, which, as the analysis is only for the purposes of comparison, and as the error is constant, can be neglected.   The detannised solution is filtered through filter paper until it is clear, and two separate quantities of 5 c.c. are titrated in the presence of 25 c.c. of indigo solution.   If the work is being systematically carried out, the extent of dilution for any particular solution will be known, otherwise a preliminary trial on the undetannised liquor must be made, and in this case it is better, at first, to dilute too much rather than too little. The final result must, in this case, be divided by the number of cubic centimetres of the original liquor which have been taken per litre, and multiplied by 1000.

It is unnecessary to dilute with distilled water, since equally accurate

[1] Supplied by the Deutsche Versuchsanstalt für Leder Industrie, Freiberg, Saxony.
[2] *Collegium*, 1907, p. 105.

results can be obtained in practice with ordinary tap-water. It is a doubtful point whether the liquor should be filtered before dilution, after dilution, or not at all. In the last case the difficultly soluble "reds," *e.g.* those of quebracho, or the catechin of gambier, are dissolved in considerable quantities on dilution, and are estimated as tannin, which cannot be entirely regarded as an error as, to a certain extent, they are utilised in tanning, if the liquors are exhausted. It is unnecessary for the purposes of detannisation to filter the liquor, but is advisable that that part of the diluted solution which is to be titrated directly should be passed through a good quantitative filter paper.

The Method of Analysis.

The systematic carrying out of the work is so arranged that the liquors to be tested are brought first thing in the morning to the laboratory and there sufficiently diluted. 100 c.c. of each of the diluted liquors are each transferred to a shaking-bottle, the necessary hide powder and kaolin added, and shaken by hand until well mixed. Simultaneously a quantity of each of the diluted liquors is filtered to remove any suspended matter. The shaking-bottles are then placed in the shaking-machine for the requisite fifteen minutes, and the contents afterwards filtered, whilst the titration of the other detannised solutions is proceeded with.

For this latter purpose, 100 c.c. of the 5 g. per litre of permanganate solution are diluted to 1 litre, care being taken to shake up sufficiently to ensure uniform mixing. Then (*a*) two separate quantities of indigo solution (25 c.c.) are titrated alone, and (*b*) the titrations repeated with the addition of 5 c.c. of freshly prepared gallic acid solution (0·1 g. to 100 c.c.) to each. The sum of the differences between (*a*) and (*b*) gives the permanganate value of 0·01 g. of gallic acid, which with the same analyst and careful work practically remains the same from day to day and need hardly be repeated every day. In the same way, 5 c.c. of the diluted liquors and then 5 c.c. of the detannised liquors are titrated in duplicate, to eliminate possible errors, and the sum of the two results taken. If the figure for the detannised liquor be subtracted from that of the original diluted liquor, the value of the 25 c.c. of indigo solution in permanganate goes out on both sides, and the permanganate value of the tannin contained in 10 c.c. of the diluted liquor is obtained. The following proportion is thus found :—Permanganate required by gallic acid is to permanganate required by liquor as 1 g. gallic acid per litre is to the number of grams of tannin in 1 litre of liquor, calculated as gallic acid. If instead of 1 g. per litre of gallic acid the weight of the tannin corresponding to 1 g. of gallic acid is substituted, the tannin content of the diluted liquor is obtained directly in grams

per litre, from which, by multiplication by the dilution factor, the content of the original liquor may be calculated. Taking 1·34 instead of 1·0, the content calculated as gallotannic acid is obtained. From about thirty analysis it has been found that the ratio of the gallic acid percentage to the gravimetric percentage is, on the average, 1·0–1·76. The following Table gives the mean numbers for the most important tanning materials determined by several analyses.

The numbers of the second series are reciprocals of the first, therefore in each case $B = \dfrac{1}{A}$.

Table 40.

Tannin Equivalents of Gallic Acid (Procter and Hirst).

A. Tannin, equivalent to 1 g. of gallic acid.		*B.* Gallic acid value of 1 g. of the respective tannin.
Chestnut wood and extract . .	1·65	0·604
Oak wood ,, . .	1·89	0·527
Myrobalans ,, . .	1·73	0·577
Mimosa extract, Quebracho and extract, average	1·69	0·592
Larch bark	1·96	0·509
Hemlock bark	1·97	0·501
Hemlock extract	2·28	0·437
Pine bark *	2·53	0·395
Mean of four fir wood tannins .	2·18	0·460
Valonia extract	1·80	0·553
Valonia	1·58	0·632
Sumac	1·53	0·650
,, ...	1·47	0·680
Oak bark	1·71	0·583
Mimosa bark	1·88	0·529
Mangrove bark	1·46	0·682
Cube gambier	1·78	0·559
Gallotanic acid	1·34	0·742
Sulphite cellulose liquors, I. .	7·75	0·129
wrongly called "Fichten- II. .	11·11	0·090
holz" extract . . III. .	7·3	0·137
Average of I. to III. . . .	8·72	0·119

* Pine bark tannin gives widely differing figures. See p. 458

If it be desired to maintain a systematic control of the liquors of a particular tannery or of a definite tanning material, this can be obtained by combining the Loewenthal method with the Standard gravimetric method (see p. 464), dependent on the difference between

"total solubles" and "non-tans." The content found by the gravi-metric method in grams per litre, divided by the gallic acid value found by the Loewenthal method, gives the required factor, *i.e.* the weight of tanning matter which corresponds to 1 g. of gallic acid.

The use of the Loewenthal method· on liquors has the advantage over gravimetric analysis not only in greater rapidity, but probably also in greater accuracy on weak liquors, as it requires no definite concentration. The figures given by Procter and Hirst show an excellent agreement. This method is also preferable for the examination of "spent" materials, as weak liquors can be analysed as accurately as strong ones, the precaution being taken to use 10 c.c. or more in every titration. Care must be taken to use sufficient water to exhaust the materials.

The gallic acid values of the different tannins are just as recognisable and constant as the iodine or saponification values of fats, and can be used as characteristic differences. An "oakwood extract," for example, with a gallic acid value of over 0·6 will really in all probability be a chestnut wood extract. Above all, however, the extremely low gallic acid value of concentrated sulphite cellulose liquors is of manifest importance.

III. APPENDIX.

1. *Estimation of Moisture.*—From 2–3 g. of tanning material are dried at 100°-110° or, preferably, at 98°-100° in vacuo, to constant weight, and the percentage of moisture calculated from the loss.

As tanning materials possess a varying proportion of moisture, according to the season of the year, the humidity of the atmosphere, etc., the moisture estimation belongs essentially to the analysis of the tanning materials. In order to compare the results of two analysts on the same material, the tannin figures must be reduced to the same water content. The percentage of tannin calculated on a hundred parts of the water-free material (dry weight) has often little value for technical purposes. Many analysts calculate the percentage of tannin to a "mean water content." According to the researches of von Schroeder,[1] the values of this latter for various tannins are as follows :—Sumac, 12 per cent.; Oak-bark, 13 per cent.; Pine-bark, Mimosa-bark, Valonia, and Quebracho-wood, 14·5 per cent.; Algarobilla and Dividivi, 13·5 per cent.; Rove, 15 per cent.; Galls, 16·5 per cent.; etc.

These calculated values are so important for the tanner that stress must be laid on the fact that they are only approximate. It is, therefore best that figures for the moisture content, as found, should always be given.

2. *Estimation of Sugary Matters.*—The tannin in the solution to be

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[1] *Gerber Zeit.*, 1888, No. 61.

examined is precipitated with lead acetate, the lead removed with potassium or sodium sulphate, the sugary matters estimated in the filtrate as described in the Section on "Alcohol, Potable Spirits and Liqueurs" (p. 739), and calculated as grape sugar.

B. The most recent Standard Gravimetric Method of Tannin Analysis, according to the Regulations framed at the Conferences of the International Association of Leather Trades Chemists.

(First, London, 1897 ; ninth, Brussels, 1908 ; tenth, Paris, 1910.)

Note.—These regulations have been for the greater part taken verbatim from the reports of the conferences. Additions have only been made where a word of explanation has seemed necessary. They are commercially the universal standard in England, and largely so on the Continent and in America, though some continental chemists still use the older "filter-method" with Paessler's "lightly-chromed" powder, which gives somewhat higher results ; in America the standard method of the A.L.C.A. differs in some unimportant particulars.

I. RESOLUTIONS OF PREVIOUS CONFERENCES STILL IN FORCE.

1. Sampling the Bulk.

With fluid extracts at least 5 per cent. of the barrels must be chosen, so that the numbers lie as far apart as possible in the series. The two upper hoops and the lid are then removed from each of these, and the contents thoroughly stirred up with a stirrer (best made of a strong wooden rod, with a circular perforated disc at the end), care being taken to remove all deposit adhering to the sides and bottom, and to mix in thoroughly. All samples must be drawn in the presence of a responsible person.

With **Gambier** and **Non-fluid Extracts**, the sample is drawn from not less than 5 per cent. of the blocks, and in such a manner that seven samples are taken from each block by means of a tube-punch which completely perforates the latter. Kathreiner made such an instrument out of brass, exactly like a cork-borer, about 36 cm. long and 3 cm. in diameters ; the mass from the tube is forced out with a wooden plunger into a flask or mortar made of heavy brass or wood, and well mixed.[1]

Solid Extracts.—5 per cent. of the bulk sample is drawn, a sufficient quantity being taken from the exterior and interior parts to give the requisite mean sample, and then broken up into small size. In the two

[1] For methods and exact description, see Procter and Parker, I.A.L.T.C. First Conference, London, 1897, p. 122 ; *J. Soc. Chem. Ind.*, 1898, **17**, 6.

last cases the sample must be mixed rapidly, and at once placed in an air-tight box, sealed, and labelled.

With **Valonia, Algarobilla,** and all **Other Tanning Materials** which contain dust or fibres, the sample must be taken as follows:—The contents of at least 5 per cent. of the sacks are tipped on to a clean, smooth floor so that they spread themselves over one another. From several places in this heap samples are drawn perpendicular to and reaching through to the floor, and these well mixed. Where this cannot be done the sample must be taken from the mean of a sufficiently large number of sacks. Whilst it is to be recommended that valonia and most other materials should be sent for analysis in a ground condition, it must be emphasised that dividivi and algarobilla should be unground.

With uncut bark, and with other tanning materials in bundles, at least 3 per cent. are sampled by cutting a section from the middle with a saw or sharp axe. Good mixing and packing is also essential in this case.

Samples which are to be submitted to more than one chemist must be drawn as a single sample, well mixed, and the necessary divisions made (not less than three), which are at once packed, sealed, and labelled.

2. Preparation of the Sample for Analysis.

Fluid Extracts must again be thoroughly mixed before weighing (the weighing should be carried out as quick as possible to avoid loss of moisture). Especial care must be taken that the sediment which is frequently deposited on the bottom of the sample bottle should be uniformly mixed in with the rest. J. Paessler[1] proceeds as follows in order to avoid loss of moisture in accurate weighings:—A stoppered weighing bottle or flask is first carefully weighed on an accurate balance, and then again on a rough balance, weighing to 0·1 g. The required weight is then placed in the scale, and the extract poured quickly into the glass. This is then closed and weighed again on the accurate balance. This process is accurate, but with practice no error arises from weighing in the ordinary way. Thick extracts, which cannot be mixed otherwise, may be warmed to 50° and stirred, but must be cooled quickly before weighing. If this method has been used it must be mentioned in the analytical report.

Solid Extracts must be coarsely powdered and thoroughly mixed.

Pasty Extracts must be rapidly mixed in a mortar, and the necessary quantity weighed out as rapidly as possible, to avoid loss of moisture.

[1] *Collegium,* 1904, p. 83 ; *J. Soc. Chem. Ind.,* 1904, **23,** 458.

III   2 G

If **Extracts** be **partly Dry and partly Moist**, so that none of the above methods can be applied, the sample must be weighed out and dried at ordinary temperatures until it can be powdered. Then it is again weighed, and the loss in weight calculated as moisture, and added to that subsequently found by drying at 100°.

In cases, such as gambier, where it is impossible to mix the constituents of the sample thoroughly by grinding, it is permitted to dissolve the whole or a large proportion of the same in a small quantity of hot water, and after thorough mixing, to weigh out a portion of the strong solution for analysis.

With barks and other solid tanning materials the whole sample, or not less than 250 g., must be ground so fine that it will pass through a sieve of four strands per centimetre or sixteen perforations per square centimetre. If materials, like many barks or dividivi, contain fibrous portions which cannot be ground so fine, the ground sample must be passed through a sieve; the part remaining on the sieve and that passed through are weighed separately, and the necessary quantities by weight of each then united for analysis.

3. Preparation of the Infusion.

The strength of the tannin solution shall be such that 100 c.c. of the same contain 0.35-0.45 g. of tanning matters.

The quantity of extract weighed out must be prescribed, so that in the event of different chemists having the same materials to analyse, they may work with solutions of the same concentration, subject to the same intrinsic errors. Thus, generally speaking, with :—

Solid extracts, quantities within the limits	5-7 g.
Pasty extracts of over 1.2 sp. gr. within the limits	9-12 g.
Fluid extracts of over 1.15 sp. gr. within the limits	12-18 g.
Fluid extracts of under 1.15 sp. gr. within the limits	18-20 g.

must be taken. The above rules provide for and must ensure that 100 c.c. of the infusion contains 0.35-0.45 g. of tanning matters.

For barks and other raw vegetable tanning materials Paessler recommends the following figures in order to obtain the requisite concentration :—Algarobilla, 9 g. ; Canaigre, 18 g. ; Dividivi, 9 g. ; Oak-bark, 36 g. ; Oak-wood, 50 g. ; Pine-bark, 32 g. ; Garouille, 16 g. ; Hemlock-bark, 32 g. ; Chestnut-wood, 45 g. ; Galls, 12 g. ; Mimosa, 12 g. ; Mangrove, 10 g. ; Myrobalans, 12 g. ; Quebracho, 22 g. ; Rove and other Galls generally, 12 g. ; Sumac, 16 g. ; Valonia, 14 g. (Trillo, 10 g.); Willow-bark, 36 g. ; Spent materials, 50 g.

Solution of Extracts.

A sufficient quantity is weighed into a covered basin or beaker, and from thence completely washed with boiling water into a litre flask. The litre flask is then filled to the mark with hot water; if all the extract is not yet dissolved, the flask is placed for a few minutes on a boiling water-bath. After thoroughly shaking, the flask is rapidly cooled to 17.5° (but not lower) in cold running water, or by other means, filled to the mark, thoroughly mixed, and at once filtered, the latter process being repeated until the filtrate is absolutely clear. The filtration may be performed with Schleicher and Schuell's extra hard filter paper, No. 605, diameter 17 cm.; but, if possible, the Berkefeld filter candle, introduced into tannin analysis by Parker and Payne, should be employed.

Whilst filter paper absorbs appreciable quantities of tannin from aqueous solution, the Berkefeld filter candle does not. The latter can be bought in various sizes, but those of 11 cm. long by 3 cm. diameter are most suitable. To free them from iron compounds and other impurities which would act upon the tannin solution, the candles are boiled with 10 per cent. hydrochloric acid, thoroughly washed out, at first with water containing hydrochloric acid,

FIG. 62.
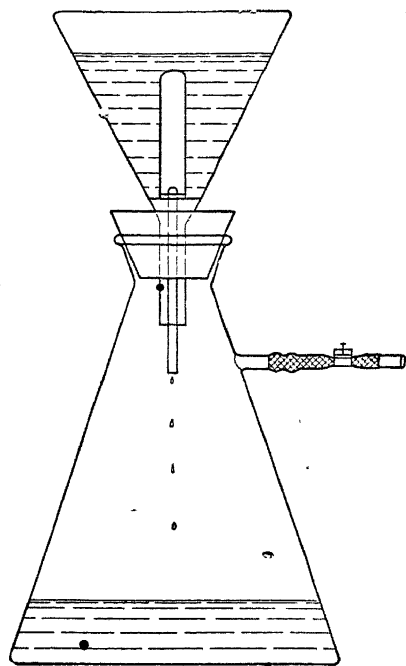
FIG. 61.

then with pure water, and finally completely dried. The filter candles are cylindrical, closed and rounded at one end, open at the other, with a cylindrical cavity down the centre. After they have been cleaned and dried, the open end of each is sealed tightly with shellac and a rubber stopper, through which passes a glass tube, which projects a few millimetres into the cavity (Fig. 62); the glass tube is then fitted into the stem of the funnel (see Fig. 61) by means of another rubber stopper.

The whole is then fitted to a filter flask, which is connected to a suction pump by means of pressure tubing. The solution can now be

filtered; it is poured into the funnel and the flask strongly evacuated (up to 40 mm.), when the pressure tubing is tightly closed by means of a screw-cock, to avoid loss by continued evaporation. In about a quarter of an hour, three-quarters to a half of the original litre of solution can be filtered. The first 250 to 300 c.c. are rejected, then about 500 c.c. are filtered, and quantities measured off for analysis. As the vacuum diminishes during filtration the loss by evaporation is lower than in the earlier methods; the funnel may be covered with a glass plate to further reduce it. Strong solutions of quebracho extract usually filter very slowly, but the rate of filtration can be materially increased by brushing the candle with a stiff brush (toothbrush), which has been washed previously in a special portion of the solution.[1] At the end of the filtration the candles are removed from their funnels and washed under the tap with the stiff brush described above. They are then replaced in the funnels, and at least 1 litre of distilled water drawn through; after drying, the candles are again ready for use. The more recent method is to use candles 11 cm. × 3 cm., and to fasten them by means of an elastic band into a funnel-like continuation of the delivery tube.[2] If candles which have previously been used for unsulphited extracts are to be used for sulphited ones, they should be previously washed with a sodium sulphite solution and then with water, to remove phlobaphenes.

Extraction of Solid Tanning Materials (Barks, etc.).

A sufficient quantity is weighed out so as to provide a solution of the prescribed strength (i.e. 0·35-0·45 g. of tanning matters per 100 c.c.). Not less than 500 c.c. of the extract must be obtained below 50°, after which the temperature is rapidly raised to 100°. The extraction is allowed to continue until the amount extracted is exactly 1 litre, and should occupy at least three hours.

The Koch extractor (bottle-extractor, see p. 456) may be used; the standard flask into which the solution flows should not be cooled during extraction.

Besides this extractor, the " syphon extractor," the so-called " beaker method" of Procter,[3] is much used by English chemists. The material to be extracted is placed in a beaker of a capacity suitable for the bulk of material to be extracted, in a water-bath. Close to the bottom of this beaker a thistle funnel is suspended, the wider end of which is covered with gauze. This is then covered with a 2 cm. layer of purified sea-sand, above which is placed the tanning material.

The tube is bent twice at right angles, thus forming a syphon, the

[1] Parker and Payne, Collegium, 1904, p. 261 ; J. Soc. Chem. Ind., 1904, 23, 648.
[2] Collegium, 1905, p. 55. [3] J. Soc. Chem. Ind., 1892, 11, 331.

longer outer end of which is further lengthened with a glass tube. This is fastened with a short piece of rubber tubing, to which is fitted a screw-cock, for regulating the flow. The tanning material is then covered with water, and allowed to soak overnight or for some hours. The water-bath is then heated, and the syphon started by careful suction ; 500 c.c. should come over before the temperature rises above 50°,[1] and then the latter is rapidly raised to 100°. The extraction is continued until the extract amounts to 1 litre, the whole process taking at least three hours. If, in special cases, the extraction by Koch's or Procter's method is incomplete with 1 litre, the second extract must be examined separately and reported as " difficultly soluble matters."

Note.—The analysis report should include :—

1. Tanning substances absorbed by hide.
2. Soluble non-tans.
3. Insolubles.
4. Moisture.

The results of any further analysis which has been made must be reported separately from the above.

Only those extracts containing less that 2 per cent. insolubles may be described as " cold soluble."

II. MOST RECENT RESOLUTIONS OF THE INTERNATIONAL CONFERENCES AT BRUSSELS (1908) AND PARIS (1910).

The Brussels Conference decided that the following "general directions," sections 1 to 4, should represent the recommendations of the International Commission on Tannin Analysis, but that the members of the I.A.L.T.C. must be also bound by sections 5 to 8.

General Directions.[2]

Section 1.—The solution for analysis must contain between 3·5 and 4·5 g. of tanning matter per litre, and solid materials must be extracted so that the greater part of the tannin is removed at a temperature not exceeding 50°, but if the Teas extractor (a metallic Soxhlet apparatus much used in America) be used, the first portion of the extract shall be removed from the influence of heat as soon as possible.

Section 2.—*The Total Solubles* must be determined by the evaporation of a measured quantity of the solution previously filtered till

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[1] If the extraction is carried out from the commencement with water at 100°, the maximum quantity of tannin is not dissolved; part is destroyed, part is fixed by the extracted material (Fiebing, Palmer and Hughes, Parker and Procter). In the examination of spent materials, where it appears impossible to obtain the prescribed concentration under the rules of the I.A.L.T.C., it is permitted to concentrate in vacuo to the required strength.

[2] *Collegium*, 1908, p. 333.

optically clear both by reflected and transmitted light; that is, a bright object, such as an electric light filament, must be distinctly visible through at least 5 c.c. thickness and a layer 1 cm. deep in a beaker placed in a good light on black glass, or black glazed paper must appear dark and free from opalescence when viewed from above. Any necessary mode of filtration may be employed, but if such filtration causes any appreciable loss when applied to a clear solution, a correction must be determined and applied, as described in section 6. Filtration shall take place between the temperature of 15° and 20°. Evaporation to dryness shall take place between 98°·5 and 100° in shallow, flat-bottomed basins, which shall afterwards be dried until constant at the same temperature, and allowed to cool before weighing for not less than twenty minutes in air-tight desiccators over dry calcium chloride.

Section 3.—*The Total Solids* must be determined by drying a weighed portion of the material, or a measured portion of its uniform turbid solution, at a temperature between 98°·5 and 100° in shallow flat-bottomed basins, which shall afterwards be dried till constant at the same temperature, and cooled before weighing for not less than twenty minutes in an air-tight desiccator over dry calcium chloride.

"Moisture" is the difference between 100 and the percentage of "total solids"; and "insolubles" the difference between the "total solids" and "total solubles."

Section 4.—*Non-tannins*. The solution must be detannised by shaking with chromed hide powder till no turbidity or opalescence can be produced in a clear solution by salted gelatin. The chromed powder must be added in one quantity equal to 6·0-6·5 g. of dry hide per 100 c.c. of tanning solution, and must contain not less than 0·2 and not more than 1 per cent. of chromium reckoned on the dry weight, and must be so washed that in a blank experiment with distilled water not more than 5 mg. of solid residue shall be left on evaporation of 100 c.c. All water contained in the powder should be determined and allowed for as water of dilution.[1]

THE FOLLOWING PARAGRAPHS GIVE THE DETAILED OFFICIAL METHOD OF CARRYING OUT THE ANALYSIS ADOPTED BY THE INTERNATIONAL ASSOCIATION OF LEATHER TRADES CHEMISTS WHICH IS OBLIGATORY ON ALL MEMBERS.

Section 5.—*Preparation of the Infusion.* Such a quantity of material shall be employed as will give a solution containing as nearly as possible 4 g. of tanning matter per litre, and not less than 3·5 and not

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[1] Anyone following sections 1-4 will be in very fair agreement with the I.A.L.T.C. method. The reason for these "general directions" is to bring the American and I.A.L.T.C. methods into general accord (Procter).

more than 4·5 g. Liquid extracts shall be weighed in a basin or beaker and washed with boiling distilled water into a litre flask, filled to the mark with boiling water, and well mixed and rapidly cooled to 17°·5; after which it shall be accurately made up to the mark, again well mixed, and at once filtered. Sumac and myrobalans extracts should be dissolved at a lower temperature.

Solid extracts shall be dissolved by stirring in a beaker with successive quantities of boiling water, the dissolved portions being poured into a litre flask, and the undissolved being allowed to settle and treated with further portions of boiling water. After the whole of the soluble matter is dissolved the solution is treated similarly to that of a liquid extract.

Solid tanning materials must be sufficiently finely ground to pass through a sieve of sixteen perforations per square centimetre (five wires per centimetre), and then extracted in a Koch (p. 456) or Procter (p. 468) apparatus with 500 c.c. of water at a temperature not exceeding 50°, and the extraction continued with boiling water till the filtrate amounts to 1 litre. It is advisable to allow the material to soak for some hours before commencing the percolation, which should occupy not less than three hours, so as to extract the maximum of tannin. Any soluble matter remaining in the material must be neglected, or reported separately as "difficultly soluble" substances. The volume of liquid in the flask must, after cooling, be accurately made up to 1 litre.

Section 6.—Filtration. The infusion shall be filtered, repeatedly if necessary, till optically clear both by reflected and transmitted light (see sec. 2). With the Berkefeld filter candle or with Schleicher and Schuell's 590 filter paper no correction for absorption is required, if a sufficient quantity (250-300 c.c.) is rejected before withdrawing the necessary quantities for evaporation; the solution may be filtered repeatedly in order to obtain a clear filtrate. If other methods of filtration are employed, the necessary average correction must be determined in the following way :—About 500 c.c. of the same or a similar tanning solution are filtered perfectly clear, and after thorough mixing 50 c.c. are evaporated, in order to estimate "total soluble" No. 1. A further portion is now filtered in exactly the manner for which the correction is to be determined (the time of contact and the volume rejected being kept as constant as possible). 50 c.c. of this filtrate are evaporated, to determine "total soluble" No. 2. The difference between Nos. 1 and 2 is the desired correction, which must be added to the weight of the total solubles found in analysis. An alternative method of determining the correction factor, which is quite as accurate and frequently more convenient, consists in filtering a portion of the tanning solution through a Berkefeld candle until

it is optically clear, which can generally be accomplished by rejecting 300-400 c.c. and returning the remaining filtrate repeatedly; simultaneously, 50 c.c. of the clear filtrate obtained by the method for which correction is required are evaporated. The difference between the weights of the residues is the required correction.

Note.—At least five determinations must be carried out in determining a mean correction. It will be found that this correction is approximately constant for all materials, and using S. and S. 605 filter paper, rejecting 150 c.c., the correction is about 5 mg. per 50 c.c.; or if 2 g. of kaolin have been used, 7.5 mg. per 50 c.c. The kaolin must have been carefully washed previously with 75 c.c. of the same liquor, allowing to stand for fifteen minutes, and then pouring off. Paper 605 has a special absorption affinity for a yellow colouring matter, which is frequently found in sulphited extracts.

Section 7.—Detannisation. Hide powder shall be of a woolly (fibrous) texture, thoroughly de-limed, preferably with hydrochloric acid, and shall not require more than 5 c.c. or less than 2.5 c.c. of $N/10$ sodium or potassium hydroxide to produce a permanent pink with phenolphthalein on 6.5 g. of the dry powder suspended in water. If the acidity does not fall within these limits, it must be corrected by soaking the powder before chroming for twenty minutes in ten to twelve times its weight of water to which the requisite calculated quantity of standard alkali or acid has been added. The hide powder must not swell in chroming to such an extent as to render difficult the necessary squeezing to 70-75 per cent. of water, and must be sufficiently free from soluble organic matter to render it possible in the ordinary washing to reduce the total solubles in a blank experiment with distilled water below 5 mg. per 100 c.c. The powder when sent out from the makers shall not contain more than 14 per cent. of moisture, and shall be sent out in air-tight tins.

The detannisation must be carried out in the following manner :— The moisture of the air-dry powder is determined, and the quantity equivalent to 6.5 g. actual dry hide powder is calculated, which will be practically constant if the hide powder be kept in an air-tight vessel. The requisite quantity of powder for the number of analyses to be performed is weighed out and soaked in about ten times its weight of distilled water. Very woolly powders require rather more than ten times their weight. For each 100 g. of dry powder 2 g. of crystallised chromic chloride ($CrCl_3 + 6H_2O$) (Kahlbaum) are dissolved in water and made basic with 0.8 g. of sodium carbonate, which is best accomplished by adding 11.25 c.c. of a normal solution, thus making the salt correspond to the formula, $Cr_2Cl_3(OH)_3$. This solution is added to the powder, and the whole churned slowly for one hour. In laboratories where many such analyses are carried out it is more

convenient to employ a 10 per cent. stock solution, made by dissolving 100 g. of the chromic chloride in a little distilled water in a litre flask, and very slowly adding a solution of 30 g. of anhydrous sodium carbonate, with constant stirring, finally making up to the mark with distilled water, and mixing well. Of this solution 20 c.c. are used for 100 g. of dry hide powder, or 1·3 c.c. for 6·5 g.

After soaking for one hour the powder is squeezed in clean linen to free it as far as possible from the chroming solution, then washed and squeezed repeatedly with distilled water until the addition of 1 drop of 10 per cent. potassium chromate solution and 4 drops of $N/10$ silver nitrate solution to 50 c.c. of the filtrate produces a brick-red colour. Four to five squeezings are usually sufficient. Thus the 50 c.c. of filtrate cannot contain more than 0·001 g. sodium chloride.

The water content of the powder is then reduced by pressure to 70-75 per cent., and the whole weighed. The quantity Q containing 6·5 g. dry powder is thus found, weighed out, and added immediately to 100 c.c. of the unfiltered tannin infusion, along with $26·5 - Q$ c.c. of distilled water. The whole is then shaken for a quarter of an hour in a stoppered rotating bottle, making not less than sixty revolutions a minute. (It can also be shaken by hand or any other suitable means.) After shaking, the powder is pressed at once in clean linen, and the solution filtered through a folded filter paper sufficiently large to contain the whole filtrate, returning it till clear; 60 c.c. of the filtrate are then evaporated and calculated as 50 c.c., or the residue of 50 c.c. is multiplied by 1·2. The non-tannin filtrate must give no opalescence with 1 drop of a solution containing 1 per cent. of gelatin and 10 per cent. of sodium chloride.

1 g. of kaolin, free from all soluble matter, must be used either by mixing it with the hide powder in the shaking-bottle, or with the liquid before filtration.

Section 8.—The analysis of used liquors and spent tans must be carried out by the same methods as those used for fresh materials, the liquors or infusions being diluted, or concentrated by boiling in vacuo, or in a vessel so closed as to restrict the access of air, until the tanning matter is, if possible, between 3·5 and 4·5 g. per litre, but in no case beyond a concentration of 10 g. per litre of total solids, and the weight of hide powder used shall not be varied from 6·5 g.

The result shall be reported as shown by the direct estimation, but it is desirable that in addition efforts shall be made by determination of acids in the original solution and in the non-tannin residues to ascertain the amount of lactic and other non-volatile acids absorbed by the hide powder, and hence returned as "tanning matters." In the case of tans, it must be clearly stated in the report whether the calculation is on the sample with moisture as received, or upon some arbitrary

assumed percentage of water; and in that of liquors, whether the percentage given refers to weight or to grams per 100 c.c.; and in both cases the specific gravity shall be reported.

Section 9.—All evaporation shall be rapidly conducted at the temperature of steam in shallow, flat-bottomed basins of not less than 6.5 cm. in diameter, to apparent dryness; and shall be subsequently dried between 98°.5 and 100° in a water or steam oven until of constant weight, and shall afterwards be cooled in small air-tight desiccators over dry calcium chloride for at least twenty minutes, and then weighed rapidly. Not more than two basins shall be placed in one desiccator, and the basins must not be wiped after removal from the desiccator.

All analyses sent out by members or associates of the I.A.L.T.C. should be made in exact accordance with the preceding regulations, and described as "Analysed according to the official method of the .I.A.L.T.C."; but if for any cause another method must be adopted, the exact method used and the reasons for its employment must be distinctly stated, such descriptions as "old official method" being prohibited. Any copy or copies of reports of analysis, whether furnished by the analyst or his client or agent, shall contain the entire matter, both written and printed, of the original report.

All analyses reported must be the average result of duplicate determinations, which must agree, in the case of liquid extracts, within 0.6 per cent., and of solid extracts, within 1.5 per cent., or the analysis shall be repeated till such agreement is obtained, and it must be clearly stated on the report that the results are the mean of such corresponding determinations.

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LEATHER

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THE subject matter of this section comprises the examination of the requisites and accessories of leather manufacture, in so far as they are not dealt with in other sections, the methods of control employed in the various processes concerned in the industry, and the methods of examining the finished product, leather.

I. ACCESSORIES TO THE PROCESSES PRIOR TO TANNING.

Water.[1]—For the purposes of tanning this should be as free as possible from the carbonates of the alkaline earths, which cause loss in the extraction of tannin and must be regarded as of the greatest importance, owing to their action on the ultimate weight and quality of the finished leather. In this respect, however, their importance has been greatly exaggerated, though their influence has not yet been sufficiently investigated. The temperature of the water certainly plays a far more important part than these dissolved mineral matters. Generally speaking, it may be said that a water containing little dissolved mineral matter is more suitable for tanning than one rich in the same; and further, that for the purposes of sole-leather tanning, it is desirable to have a water of constant low temperature, while for upper leather one with not too low a temperature is to be preferred. Doubtless also the presence in the water of living organic matter, such as bacteria and yeasts, and of unorganised ferments, the so-called "enzymes," has a determining influence on the quality of the leather; but on this point little or no research has been carried out.

Extremely hard water also acts deleteriously during the preliminary treatment of hides and skins, in which the removal of hair is accomplished by liming or the use of sodium sulphide. Calcium carbonate is precipitated through the hairs on to the grain, and is difficult to remove in the subsequent deliming processes. These "water blasts" are

[1] *Cf.* F. Simand, *Gerber*, 1889, **15**, 205.

particularly fatal to finer leathers which are to be dyed, and especially to glacé leather; the damage is observable in the undyed leather as rough dull patches, and in the dyed leather as lighter areas on which the colour has taken irregularly.

It is difficult to use waters containing much organic matter in the tannery, as they are generally rich in putrefactive organisms; if, in the absence of any other supply, such waters must be used, great care must be taken, especially during the washing and soaking processes. The danger lies in the fact that the putrefactive organisms may settle upon the hide and attack it, and they are especially injurious to the grain. These defects are observable in the finished article in the marking or breaking of the grain, pock marks, pin holes, weak grain, etc.

Depilatories.—The following processes are used for unhairing:— "Sweating," i.e., a carefully controlled putrefactive process, in which the ammonia liberated probably acts as the depilatory; "Liming," by laying or suspending in a milk of lime; or "Lime paste," painted on the flesh side. To strengthen the action of the lime liquor or paste, it is frequently mixed with sodium sulphide, calcium sulphydrate, or realgar (arsenic sulphide).

(a) *Caustic Lime.*—For this purpose a lime as rich as possible in CaO, but containing little magnesia, alumina, or silicates, should be used. For the estimation of the content of lime, see Vol. I., p. 483.

(b) *Sodium Sulphide.*—The commercial crystallised salt, $Na_2S + 9H_2O$ (32·5 per cent. Na_2S and 67·5 per cent. water), has a colour varying from wine-yellow to dark brown or green; most commercial varieties are but little adulterated, though particles of carbon, sodium sulphate, and thiosulphate are often present. Anhydrous varieties are now, however, being sold which are generally less pure. The content of sodium sulphide is determined by titration with an $N/10$ ammoniacal zinc sulphate solution, using cobalt paper or a lead salt as indicator (spotting method); or, according to Simand, by titration of the solution with $N/2$ hydrochloric acid in the presence of phenolphthalein until the red colour is permanently discharged. In this last case exactly half the sodium which unites with the sulphur to form sodium sulphide is estimated ($Na_2S + H_2O = NaHS + NaOH$). If methyl-red, or orange, or Congo red is used as indicator, the whole of the base is estimated. A further alternative method is to titrate the sodium sulphide solution, first directly, and then after precipitation with zinc sulphate, with an iodine solution of known strength; the difference of iodine solution required for the two titrations is calculated to sodium sulphide from the equation, $Na_2S + I_2 = 2NaI + S$.[1] (*Cf.* also Vol. I., p. 437.)

(c) *Calcium sulphide, Calcium sulphydrate.*—These substances usually

[1] J. Paessler, "Die Untersuchung der Schwefelnatriums." *Cf.* also F. Jean, *Ann. Chim. anal.,* 1897, **2,** 341 ; *J. Soc. Chem. Ind.,* 1897, **16,** 1041.

come into commerce as waste- or by-products of the Le Blanc soda process, as, for example, "calcin," the so-called "liming compound." The reactive principle of this material is a polysulphide, the method of estimation of which is given in Vol. I., p. 437.

(d) *Arsenic sulphide compounds : Yellow Arsenic (Orpiment), Red Arsenic (Realgar).*—These arsenic sulphide compounds are generally mixtures of red and yellow arsenic. J. von Schroeder and W. Schmitz-Dumont[1] have shown that the activity of these compounds depends on their double decomposition with lime to form calcium sulphydrate, and the active principle is therefore sulphur. The estimation of the value of arsenic sulphide compounds consequently comprises simply a determination of the sulphur, which can be carried out by any of the well-known methods, such as oxidation with fuming nitric acid and precipitation with barium sulphate. (*Cf.* Vol. I., p. 281.)

It is to be borne in mind, however, that it is only the sulphur that is liberated as sulphuretted hydrogen by acids which acts directly on the hide. (Procter.)

Deliming, Swelling, and Bating Materials.

To remove the lime from the hide and to prepare it for tanning proper, as, for example, by swelling the pelt (the name given to the unhaired hide ready for tanning) if intended for sole leather, inorganic acids (sulphuric and hydrochloric) and organic acids (formic, acetic, butyric, and lactic) are used, as well as so-called "bates," of which the action is bacterial and fermentative, made with bran, dung, and similar materials, and artificial bates (" Erodin " of Popp and Becker, " Oropon " of Roehm, " Purgatol " of Eberle), depending on bacterial or enzyme action.

The amount of acid available for deliming and swelling is determined by titration, and should be as free as possible from iron compounds. In lactic acid, which is usually sold in 40 per cent. solution, but more recently in 70 per cent., the amount of anhydride which is always present must be taken into consideration.

This is estimated in the following manner :—10 g. of the acid are diluted with distilled water to 500 c.c. 50 c.c. of this solution are poured into a porcelain basin and titrated with $N/2$ alkali in the presence of phenolphthalein to a permanent pink; then, according to the strength of the acid examined, 1-3 c.c. of $N/2$ alkali in excess are added, boiled for a short time, and, after cooling, titrated back with $N/2$ acid until the red colour disappears. Besson[2] states that if the alkaline solution be warmed or boiled a higher result is obtained, owing to the action on other substances, and recommends that after the addition of

[1] *Dingl. polyt. J.*, 1896, 300, 161 ; *J. Soc. Chem. Ind.*, 1896, 15, 549.
[2] *Collegium*, 1910, p. 73 ; *J. Soc. Chem. Ind.*, 1910, 29, 440.

the alkali the solution should be allowed to stand for ten minutes at room temperature. From the total quantity of alkali added minus the amount of acid required to titrate back, the " total lactic acid " (lactic acid and anhydride) can be calculated. From the amount of alkali required for the first titration, the amount of " free lactic acid " (lactic and anhydride) can be calculated.

These values are only accurate if the commercial lactic acid contains no other free acids. As lactic acid is always produced by the action of sulphuric acid on calcium lactate, a qualitative test for free sulphuric acid is necessary, for which Eberhard recommends the following procedure :—1 part of the lactic acid is well shaken up with 5 parts of 95 per cent. alcohol in a test tube. After standing for a quarter of an hour 5-10 c.c. are filtered off, and to the clear solution a few drops of calcium chloride solution, acidified with hydrochloric acid, are added. In the presence of free sulphuric acid a turbidity soon appears. For the quantitative estimation the total sulphuric acid (a), and the sulphuric acid found in the residue on incinerating (b), and lastly, that present as ammonium sulphate, must be determined. From the difference between that estimated under (a) and that estimated under (b) and (c), the amount of free sulphuric acid is found.

For the purposes of the tanner, lactic acid should be free from hydrochloric and oxalic acids. The distillate should therefore give no chlorine reaction, and no turbidity with calcium chloride solution.

The raw materials of the bran, dung, and artificial bates do not admit of any commercial chemical tests.

II. Vegetable Tanning Materials and Tannin Infusions.

For the estimation of tannin, see the previous section, pp. 453 *et seq.*

To differentiate the infusions of the different tanning materials certain characteristics may be employed. Infusions of barks have generally a higher ash than those of woods, although these differences, owing to the present frequent treatment of extracts with mineral salts, are hardly reliable. The tanning contents found by the gravimetric and the Loewenthal methods are in much closer accord with extracts of woods than with those of barks. Conclusions may consequently be drawn from determinations by both methods, although, owing to the present treatment of extracts with chemicals, this is becoming daily more uncertain. Quebracho wood extract, if it is pure and has undergone no other treatment, and when residual substances, such as difficultly soluble matters, have been removed, can be recognised in that in 100 parts of moisture-free extract there are 85-95 parts of tanning substances, as determined by the gravimetric method. For

some years' cold soluble quebracho extracts have been coming on to the market, which by treatment with chemicals, generally with sulphites or bi-sulphites, have been made completely soluble in water at ordinary temperatures without residue; such extracts may contain up to 10 per cent. of mineral matter. Sumac extract has a peculiar tea-like smell; chestnut-oak extract shows a fluorescence in the hide powder filtrate; mimosa bark extract in very dilute, clear, filtered solution, according to Simand, gives with 1 drop of baryta water, when carefully allowed to drop on to the surface, a greenish-blue precipitate which rapidly becomes reddish-brown.

An addition of myrobalans extract to quebracho extract can be detected by the Stiasny reaction[1] with formaldehyde and hydrochloric acid. For this test 50 c.c. of the quebracho extract solution of the strength required for tannin analysis is boiled with 10 c.c. of dilute hydrochloric acid and 10 c.c. of formaldehyde for about thirty minutes under a reflux condenser. The quebracho extract is thus precipitated, whilst the myrobalans tannin, if present in appreciable quantity, remains in solution as pyrogallol tannin, and can be recognised in the filtrate by the violet-coloured solution produced on the addition of sodium acetate and a few drops of iron alum. For the differentiation of tanning extracts, Philip recommends the ammonium sulphide reaction proposed by Eitner and Meerkatz[2] for chestnut and oak wood extracts, which Simand has also applied to other tanning extracts. By dilution with water the extract is brought to about 2 per cent. tannin content, then 100 c.c. of this solution are boiled for a few minutes with the addition of 0.5 g. of concentrated sulphuric acid. After cooling, 20 g. of sodium chloride are added, and the solution filtered; 15 c.c. of distilled water are mixed with 10 drops of yellow ammonium sulphide in a test tube, and 1.5-2 c.c. of the filtrate added, well shaken up, and allowed to settle. The precipitate of chestnut wood extract is at first brownish, then reddish with a blue sheen; with oak wood extract it is yellowish-brown, and the supernatant solution Bordeaux red to orange. In this test it is advisable to do a blank test simultaneously with a really pure oak wood extract. Other extracts give the following precipitates by this method :—

Oak bark, first yellowish, later fawn-brown.
Valonia, first yellowish-green, later chamois.
Galls, first yellowish, later reddish-brown.
Myrobalans, first greenish, remains unchanged.
Dividivi, bright greenish-yellow, remains unchanged.
Hemlock bark, after a long time yellowish-brown.
Mallet bark, yellowish-brown.
Mimosa bark, pink (reddish-white).

[1] *Gerber*, 1905, 31, 186.　　　[2] *Ibid.*, 1885, 11, 157.

No precipitate is formed with the following extracts :—

Quebracho wood, mangrove bark, pine bark, catechu, and gambier; pine bark occasionally gives a slight turbidity, and a few cold, soluble quebracho extracts give a slight brownish precipitate.[1]

Paessler[2] has shown that colouring wool strips, which have been printed with different metallic salts (the so-called garancine strips), show recognisable differences with most tannins. If several such strips be coloured in the same bath, mixtures of different tannins can be frequently recognised, as one tannin acts more quickly on the strip than another, and the strips show varying colour shades.[3]

III. MINERAL TANNING MATERIALS.

Of these only aluminium and chrome salts find practical application in leather manufacture, the first in white or alum tanning, the latter in chrome tanning.

(a) In *Alum Tanning*, potash alum, soda alum, or aluminium sulphate with common salt, are principally used. The tanning value of these alumina salts, which should be as free as possible from iron, is determined by estimating the contained Al_2O_3 by the method described in the section on "Aluminium Salts and Alumina," Vol. II., p. 610.

(b) *Chrome Tanning* is accomplished either by means of chromium salts (one-bath method) or by treatment with alkali chromates in acid solution and the subsequent reduction of the chromic acid by means of sodium thiosulphate (two-bath method). In the first case the reactive principle is the basic chrome salts, which are best utilised when about one-third basic, and which tan of themselves; in the latter case they are first produced in the reducing bath, and only then accomplish the tanning of the hide fibre. For the production of the basic chromium salts (usually the sulphate or chloride) either chromium hydroxide or chrome alum may be used, or the concentrated chrome extracts specially prepared for the purpose may be employed. These latter, in addition to basic chromium salts of inorganic or organic acids, usually contain a greater or less quantity of foreign substances, such as alkali salts, alumina salts, etc. The estimation of chromium salts and chromates is described in the section on "Metals other than Iron,"

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[1] For a careful study of the qualitative determination of tannins, see Stiasny and Wilkinson, *Collegium*, 1911, pp. 318 *et seq.* Much advance in the qualitative detection and separation of tannins has recently been made, and for the latest information the pages of recent issues of *Collegium* must be consulted. *Cf.* also *Leather Chemists' Pocket Book*, pp. 47 *et seq.*

[2] *Collegium*, 1906, p. 287.

[3] Synthetic or artificial tannins, and especially Dr Stiasny's "Meradol D.," have attained considerable commercial importance. They are mostly sulphonated condensation products of phenols with formaldehyde. The waste liquor of sulphite-cellulose manufacture is now largely used as an adulterant or addition to extracts.

Vol. II., pp. 363 *et seq.* The thiosulphate estimation is carried out iodometrically (see Vol. I., pp. 117 and 438).

IV. Other Tanning Materials and Accessories for Leather Dressing.

Marine animal fats, especially fish oils, are utilised in chamois-leather dressing, also egg yolk, common salt and flour with alum in glacé leather dressing, tallow in admixture with oils and mœllon (degras or sod oil) in fat tannages used to stuff different kinds of leather and increase their suppleness. For the latter purpose neats-foot oil and bone oil are much used, whilst soap serves for the preparation of soap, pastes, fat liquors, etc.

Preserved Egg Yolk.—Egg yolks (hen or duck) recovered from the albumin manufacture are preserved with common salt or boric acid (also borax), or with both together (more recently also with fluorides), and provide an important accessory in glacé kid and chrome tannages. An endeavour was made[1] to dry out the egg yolks, but appears to have been too costly or unsatisfactory, as the preparation did not remain long on the market. The value of preserved egg yolk is usually estimated by the moisture content, the egg-oil content, and the amount of sodium chloride or other preservative present. The I.A.L.T.C. has prescribed the following method for the examination of egg yolk :—

(*a*) *Moisture.*—From 10-20 g. are weighed out into a flat-bottomed basin, together with a small glass rod and a little ignited sand, thoroughly stirred at the ordinary temperature, and dried at 100°-105° to constant weight.

(*b*) *Egg Oil; Fat.*—The residue from the moisture estimation is broken up into small pieces, and extracted in a Soxhlet apparatus with petroleum spirit boiling between 70°-75° until the petroleum spirit in the extraction vessel becomes colourless; then the residue is broken up and again extracted. After the extraction is complete, the petroleum spirit is distilled off from the previously weighed flask, and the residue (egg oil) dried for an hour at a 100°-105°. In the statement of results the solvent used should be stated.

If the yolk contains free boric acid a certain proportion is extracted by the solvent for the fats. To remove this the solution of the fat is shaken out two or three times successively with distilled water at 30° in a separating funnel, the aqueous solutions united, 20 c.c. of neutral glycerol and a few drops of phenolphthalein added, and the solution titrated with normal alkali (1 c.c. normal alkali = 0·0613 g. boric acid), and the amount found subtracted from the amount of fat.

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[1] *Gerber*, 1875, I, No. 32.

(c) *Sodium Chloride.*—The residue from the fat extraction is freed from petroleum spirit, placed in a funnel with a small asbestos filter, which is fitted to a 250 c.c. flask, and lixiviated with hot water. An aliquot part of the solution, which has been made up to 250 c.c., is titrated with $N/10$ silver nitrate in the presence of potassium chromate.

(d) *Total Ash.*—5 g. of egg yolk are dried in a platinum basin, and the residue after the extraction carefully ignited at low red heat. If the proportion of ash exceeds that of the sodium chloride content by more than 1·5 per cent., borax and other mineral matters must be tested for.

(e) *Boric Acid and Borax.*—These can be qualitatively recognised by digesting the egg yolk with sulphuric acid, adding methyl or ethyl alcohol, and obtaining the green-edged flame.

For the quantitative estimation, 5-10 g. of egg yolk are made alkaline with potassium hydroxide, dried, and the residue after extraction ignited. The alkaline ash is dissolved in a small quantity of hot water, rendered faintly acid with hydrochloric acid, and boiled for a few minutes under a reflux condenser to expel carbon dioxide. After cooling, the solution is neutralised with normal alkali in the presence of phenolphthalein, 20 c.c. of neutral glycerol added and titrated to a permanent pink colour, which should not disappear on the addition of more glycerol. 1 c.c. of normal alkali is equivalent to 0·0613 g. of boric acid. K. Windisch[1] recommends the addition of mannitol in the place of glycerol.

(f) *Fluorides* can be recognised by gently heating a not too small amount of the egg yolk with concentrated sulphuric acid in a platinum crucible, and observing the etching produced on a glass plate placed above.

Admixture of Other Oils.

The accurate recognition of other oils in egg yolk presents great difficulties. Vignon and Meunier[2] propose to determine the iodine value, the unsaponifiable matter, and the total phosphoric acid in egg oil extracted with chloroform, and from these values to form conclusions as to the addition of other oils. They have established the following values for egg oil :—

	Hen-egg yolk.	Duck-egg yolk.
Iodine value	48·7 to 54·8 (mean 52)	35·4 to 39·25 (mean 37·4)
	Per cent.	Per cent.
Unsapofiifiable matter . . .	0·16 to 0·23	2·43 to 2·85
Phosphoric acid (H_3PO_4) . .	2·33	1·91

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[1] *Z. Unters. Nahr. u. Genussm.*, 1905, 9, 659.   [2] *Collegium*, 1904, p. 35.

That these values are not absolutely constant, the following figures by Paessler show, which have also been obtained with egg oil extracted with chloroform.

	Hen-egg yolk.	Duck-egg yolk.
Iodine value	42 to 48·1 (mean 45·9)	54·2
	Per cent.	Per cent.
Unsaponifiable matter . . .	3·1 to 3·8 (mean 3·4)	6·2
Phosphoric acid (H_3PO_4) . .	3·7	3·1

To estimate the phosphoric acid 2 g. of egg oil are weighed into a platinum crucible, 6 g. of an oxidising fusion mixture (consisting of 2·5 parts of sodium carbonate, 2·5 parts of potassium carbonate, and 5 parts of potassium nitrate) added, heated slowly over a Bunsen burner until the whole of the carbon has disappeared, and the phosphoric acid determined either volumetrically with uranium nitrate, or gravimetrically.

The methods for the determination of the saponification, iodine and acid values of oils are described in the section on "Oils, Fats, and Waxes," this Vol., pp. 114 *et seq.*

It is apparent from the above figures that any conclusions from the values obtained must be drawn very cautiously.

The preserved egg yolk of commerce has approximately the following constituents (mean and extreme values) :—

	Preserved only with salt, or with salt and boric acid.		Preserved only with boric acid.	
	Mean per cent.	Extreme per cent.	Mean per cent.	Extreme per cent.
Water	51·0	47 to 54	50·0	47 to 53
Mineral matters . .	15·0	12 ,, 18	2·0	1·5 ,, 2·5
Egg oil . . .	21·0	17 ,, 25	30·0	27 ,, 33
Albumins . . .	13·0	9 ,, 17	18·0	14 ,, 22
	100·00		100·00	
Sodium chloride . .	13·5	10 to 17	...	...
Boric acid . . .	1·0	0 ,, 2	2·5	1·5 to 3·5

Preserved egg yolk should have a clear orange-yellow colour, and should be homogeneous; the smell should be fresh and pleasant.

Tallow.[1] — The examination and characteristics of tallow are described in the section on "Oils, Fats, and Waxes," this Vol., p. 152. Tallow for the purposes of leather dressing should contain no

[1] *Cf.* Schmitz Dumont, *Dingl. polyt. J.*, 1895, **296**, 210, 233, 259; *J. Soc. Chem. Ind.*, 1895, **14**, 815, 829.

free sulphuric acid. For stuffing upper leathers soft tallow is to be preferred, as it is not so liable to form white incrustations on the leather (these are due to high melting point palmitins and stearins). For those kinds of leathers which are stuffed by immersion or drumming in melted fats, such as belting and harness leather, a tallow with a high melting point, such as sheep or pressed tallow, may be used.

Fish Tallow, a by-product of the oil recovery from fish (the fish are chopped up into small pieces and pressed while hot; the oil so obtained deposits fish tallow at a low temperature), should contain none or little of the gelatinous materials present during recovery. For their estimation 20 g. are warmed with 150 c.c. of petroleum spirit, filtered through a weighed and previously dried asbestos filter-tube, the residue repeatedly washed, the tube dried and then weighed. Frequently 6 per cent. and more of these non-fats are found. They do not penetrate the leather, but remain on the surface as sticky masses; the smaller the quantity of these the more utilisable is the fish tallow.

Fish Oils.—Fish oils provide in their original state or in oxidised modified forms, such as moêllon and dégras produced during chamois-leather dressing or by special processes, the most important fatty material of the leather industry. They serve, on the one hand, in chamois-leather dressing as the tanning material proper; on the other hand, in currying as the most important stuffing material.

The following fish oils have mainly to be differentiated :—

1. *Blubber Oils*, from the blubber or entire bodies of the sea mammalia : seal oil, whale oil, dolphin oil, porpoise oil.

2. *Liver Oils*, from the livers of fish : cod and shark oils.

3. *Fish Oils proper*, obtained by pressing the entire fish : herring, sardine (Japan), and menhaden fish oils.

The various oils are differentiated in commerce according to their colour after recovery, viz. :—Pale brown and black.

It is extremely difficult to distinguish fish oils derived from different sources. In the literature of the subject methods can indeed be found by which the fish oils can be distinguished from one another and from other oils by certain colour reactions which they give with sulphuric acid, phosphoric acid, nitric acid, or sodium hydroxide. More recent researches by Holde[1] and by Lewkowitsch[2] have shown that these older methods are not reliable. The latter has pointed out that every coloration is characteristic not of the oils themselves but of their impurities, and these can be removed by treatment, so that the pure materials do not give the colour reactions; consequently their value is very small.

Shark oil is recognisable by its high percentage of fluid waxes, and

[1] *Mitt. tech. Versuchsanstalt*, Berlin, 1890, 8, 19.   [2] *J. Soc. Chem. Ind.*, 1894, 23, 617.

consequent high unsaponifiable value, which may be as high as 15 per cent. The unsaponifiables are very imperfectly shaken out with petroleum spirit, and ethyl ether should be used for the purpose.

According to V. Boegh[1] shark oil, or the addition of this oil to others, can be recognised by the difficult solubility of its soaps, and he describes the following method of examination :—10 g. of the oil to be tested are saponified in a flask with 50 c.c. of alcohol and 10 c.c. of a solution of sodium hydroxide (362 g. NaOH per litre) on the water-bath —with the addition of a reflux condenser if necessary—and after the saponification is completed the solution is evaporated to dryness. Boiling distilled water in a series of measured quantities is then added, first 50 c.c. and then 5 c.c. at a time, whilst the flask is kept hot on the water-bath and thoroughly well shaken, until it becomes obvious that no more is dissolved; the amount of water required is then noted. If this is more than 70 c.c., then it is to be concluded that the oil is mixed with shark oil.

The density of fish oils at 15° varies from 0·914-0·935, and the refractive index (determined with Abbè's refractometer) from 1·471-1·481; generally speaking, a high density is accompanied by a high refractive index. The melting point of the fatty acids lies between 10° and 38°, and if the fish oil has a high density its fatty acids have usually a high melting point. The fatty acids of fish oils have ordinarily a melting point above 30°. Fish oils always contain free fatty acids; usually the greater their quantity the darker is the oil.

According to Eitner two fish oils, light and heavy, are to be distinguished in practice. Light fish oils are those of low specific gravity which are fluid and usually light coloured; by reason of their low stuffing power they are also called "thin oils." They do not easily combine with the leather fibre, but penetrate quickly and strike through. In chamois dressing, which is dependent on the oxidation of the fish oil and subsequent combination of the same with the hide fibre, they act either quite inefficiently or not at all. They show a great tendency to form a resinous incrustation on leather stuffed with them. The heavy fish oils of high specific gravity consist either of a light fluid fat, containing much dissolved palmitin (herring or sardine oil), or more frequently of a thick, fluid, fatty substance (liver oils), which, with the exception of shark liver oil, are regarded as the most valuable variety used in tanning and stuffing operations.[2]

As the differentiation of fish oils is so difficult, their investigation is mostly limited to the determination of their suitability for a definite

[1] *Collegium*, 1924, pp. 73 and 88.

[2] For the examinations of fish oils, fats, etc., see also the section on "Oils, Fats, and Waxes" in this Vol., pp. 105 *et seq.*

process, and to tests for admixture of foreign matters, such as mineral or rosin oil, etc.

The density and refractive index can be used as qualitative tests for the presence of mineral and rosin oil in fish oil. Rosin oils, of which only the denser need be considered, have a sp. gr. of 0·980-0·996, the refractive index lies between 1·532-1·552; with vaseline (petroleum) oils these values are 0·890-0·910 and 1·490-1·509 respectively. By the addition of rosin oil the specific gravity and refractive index are raised; vaseline oil lowers the specific gravity and raises the refractive index. The adulteration of fish oils with rosin and vaseline oils is usually great, so that their detection is easy. By determination of the specific gravity and refractive index of an adulterated fish oil, the extent of the falsification can be estimated within certain limits (10-15 per cent.), and a close guess made as to the actual quantity added.

If it cannot be concluded with certainty that an oil has been adulterated from a determination of its specific gravity and refractive index, qualitative saponification tests must be made, which always give some indication; for this purpose, 10 g. of fish oil are saponified with 3 g. of sodium hydroxide in 5 c.c. of water and 40-50 c.c. of alcohol, under a reflux condenser. The resulting soap is not completely soluble in aqueous alcohol (1 : 15) if much of the adulterant has been added; if little, the solution is tolerably clear, especially with petroleum oils. The soap is decomposed with dilute hydrochloric or sulphuric acid, and the fatty acid, etc., washed on a wet filter with hot water; a portion is then dissolved in 3 or 4 vols. of alcohol, in which it will dissolve completely, if but little vaseline oil has been added (if much, it is impossible to dissolve the whole in the given volumes of alcohol), and made feebly alkaline with ammonia. A distinct turbidity appears if the fish oil contains only a few per cent. of unsaponifiable matter, and only a few particles are left or the solution remains clear if the oil is pure. If the precipitated soap solution is diluted with an equal quantity of water, the unsaponifiable oils appear after some time as drops on the surface.

If it is desired to estimate the unsaponifiable matter quantitatively, a weighed quantity of the oil (10 g.) is saponified in a flask fitted with a reflux condenser with 5 g. of sodium hydroxide dissolved in a few cubic centimetres of water and 50 c.c. of alcohol; from half to one hour is required with normal oils for the saponification, or one and a half to two hours with difficultly saponifiable oils, while liquid waxes, such as sperm oil, cannot be completely saponified in this way. The glycerine soaps, after dilution with 50 c.c. of water, are poured into a separating funnel, the flask washed with 100 c.c. of petroleum spirit (which should contain no fraction boiling above 70°), and shaken thoroughly; the shaking out is then proceeded with. The solution is shaken out three

times successively with 75-100 c.c., which is amply sufficient. It is to be recommended that in the first shaking out the fluids should only be mixed with a gentle rotary motion, to avoid the formation of a permanent emulsion. In spite of this, even with very careful shaking, emulsions are liable to be formed; these can, however, be rapidly broken up by the addition of a few cubic centimetres of hot alcohol. The petroleum spirit layer is separated, and, to remove dissolved soap, is shaken up three times for five minutes each with a quantity of water equal to about one-fifth of its volume; the petroleum spirit is then distilled off on the water-bath. The residue, the unsaponifiable matter, is washed without loss by means of a small quantity of petroleum spirit into a small weighed flask, and after removal of the solvent at 100°-105°, dried to constant weight, which should be completed within from half to one hour. This method has been shown to be very satisfactory.

The following method also gives accurate results:—10 g. of fish oil are saponified as above, dissolved in water, the greater part of excess of alkali neutralised with hydrochloric acid, and barium chloride, calcium chloride, or lead acetate added in slight excess, the barium, calcium, or lead soaps being precipitated in the cold. These are drained upon a filter with the help of the pump, washed with dilute cold alcohol (1 : 20) and dried in a vacuum desiccator on blotting-paper. The dried soaps, mixed with sand, are then extracted for six hours in a Soxhlet extractor with chemically pure, water-free, freshly distilled acetone, or petroleum spirit which should contain no fraction boiling above 75°. After the solvent has been distilled off, the unsaponifiable matter and a little water remain behind; these are then dissolved in a little petroleum spirit, and poured into a separating funnel; the subsequent procedure is then as usual.

The content of fish oils in oxidised fatty acids (Simand describes these as "dégras-former") varies from 0·1-6 per cent. Oils with a high specific gravity and refractive index generally contain a correspondingly large amount of hydroxy fatty acids. Old fish oils have, as a rule, a high percentage of these acids. For the estimation of oxidised fatty acids, see under "Dégras" (p. 490).

The ash of a fish oil should be as free as possible from iron,[1] as otherwise the leather treated with it is liable to be stained. Considerable quantities of iron are frequently present in the form of iron salts of fatty acids; these are not absorbed by the leather, and darken its surface.

The addition of cotton-seed oil to fish oils causes, by reason of the high melting point of its fatty acids (34°-38°), a corresponding raising of the melting point of the fatty acids of the mixed oils; and as fish oils containing fatty acids with high melting point associated with

[1] Cf. Simand, Gerber, 1890, 16, 205.

high specific gravity also show a considerable content of oxidised fatty acids when not containing cotton-seed oil, it may be concluded, according to Simand, that a high melting point of the fatty acids with a low content of oxidised fatty acids and low specific gravity is due to the presence of unoxidised cotton-seed oil. The chief adulterants for fish oils, however, are always vaseline oils, and in considering possible adulterants it is well to consult a current price-list.

The Greenland "Three Crown" fish oil is a mixture of different sorts of oils, chiefly seal and shark oil, with occasionally whale oil. The Swedish "Three Crown" fish oil is a mixture of various seal and fish oils.

A fish oil, for use in leather stuffing, should not have too high an iodine value, as it renders the leather liable to "spue"[1] as the result of oxidation (see further under "Dégras," p. 489). Fish oils with a high iodine value lose their tendency to spue after prolonged boiling, therefore any oil with an iodine value of over 130 should be treated in this manner.

Simand has pointed out that so-called *Sea-Lion Oil* consists of rosin oils (the ordinary common varieties of sp. gr. 0.996) which have been mixed with 10-30 per cent. of a very rich fish oil to produce the characteristic smell.

Neat's-foot and Bone Oil.—Both these oils are much used in the preparation of fat liquors for chrome leather, and must, therefore, be free from solid fats to avoid spueing. In order to fulfil these conditions completely, these oils must be "cold-stable," *i.e.*, they must give no deposit on standing at a low temperature. It is usually demanded of these oils that they should be cold-stable at minus 10°. H. Becker[2] describes the following method of testing:—A test tube 18 mm. wide is filled with a sample of the oil to be tested, which has been dried by means of calcium chloride and subsequent filtration through a dry filter paper. A bored cork fitted with an accurate thermometer is placed in the test tube so that the bulb is in the middle of the layer of oil. Then this sample is placed, together with a similar undehydrated sample, in a freezing mixture, which is at the guaranteed minimum temperature. Neat's-foot oil passes this cold test if it remains completely fluid and clear at the end of one hour.

Moëllon and Dégras.[3]—Originally these terms were only applied to the product resulting from the oxidation of fish oil in chamois dressing, which finds much application in the leather industry as a stuffing mixture; from good samples of this kind water should not be

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[1] To "spue," in this sense, is to produce on the leather resinous spots of oxidised oil. The spueing referred to later as produced by neat's-foot and bone oil is merely a whitish deposit caused by the crystallisation of hard fatty acids.

[2] *Collegium*, 1907, p. 393.   [3] Cf. *Collegium*, 1906, p. 304.

deposited even after long standing. Moëllon and dégras contain water (about 8-20 per cent.) and 5-20 per cent. of a substance (not containing nitrogen, as Simand assumed) which is produced during chamois dressing, and is characteristic of. all these materials. F. Simand[1] called this substance "dégras-former," and F. Jean[2] "resinous matter" or "dégragène." W. Fahrion[3] has proved that it consists simply of oxidised fatty acids (in chamois dressing produced by the action of the oxygen of the air on the unsaturated acids and their glycerides), and describes it shortly as "oxy-acids." These oxidised acids and their glycerides enable the fish oil to form emulsions with water in almost all proportions; this property is the conditional factor which enables moëllon and dégras to penetrate the leather during stuffing and spread easily and uniformly throughout. They are therefore absorbed as watery emulsions of more or less strongly oxidised fish oil. They emulsify the more easily the higher the proportion of contained oxidised fatty acids, though according to Fahrion this is limited by their increasing viscidity. If the oxidation of the fish oil in chamois dressing proceeds too far (i.e. to a too high oxidised fatty acid content) nitrogenous substances of a syrupy gelatinous nature also come out of the pelt with the dégras, which are only slowly and incompletely absorbed by the leather. Good samples of moëllon and dégras produce a certain "feel" in the leather which is described as "mellow."

Moëllon and dégras have essentially a lower iodine value than the fish oil from which they have been derived. This is not only due to the oxidation during chamois dressing, but also to a polymerisation of the unsaturated fatty acids. This lowering of the iodine value is so far of importance in that it opposes the tendency of the fish oil or its products to oxidise in the leather and so cause spueing. According to Fahrion the iodine value of a moëllon or dégras (calculated on the dry weight) should not exceed 100.[4]

The oxidised fish oil is recovered from the treated chamois leather either by moderately powerful pressure (when the resulting product is described as "moëllon": French or pressure process), or by washing out the leather with alkaline carbonates, thus converting the material into a thin emulsion out of which the dégras is recovered by treatment with sulphuric acid (German process). Very frequently a combination of both methods is used. The moëllon is always more or less fluid; the dégras is generally thicker owing to the presence of soaps (3-4 per cent. on the water-free weight) and of leather fibres. In commerce these differences are no longer strongly marked.

[1] Gerber, 1890, 16, 243. [2] Monit. Scient., 1889, 15, 889.
[3] Z. angew. Chem., 1891, 4, 172; Chem. Zeit., 1893, 17, 524; J. Soc. Chem. Ind., 1891, 10, 557; 1893, 12, 937.
[4] Cf. Fahrion, Chem. Zeit., 1891, 15, 1791; 1892, 16, 862; J. Soc. Chem. Ind., 1892, 11, 183.

Water in Moêllon and Dégras.—For this determination, according to Fahrion, 2-3 g. are weighed into a platinum crucible without a lid, and the water boiled off at once by means of a small Bunsen flame, which is carefully and repeatedly applied to the crucible and withdrawn. The point at which all the water has disappeared is denoted by a low crackling and a wisp of smoke, and with a little practice can be most accurately observed. The moisture content varies with the sample, in the French process from 8-20 per cent, and with dégras from about 20-40 per cent.; over 25 per cent. could not therefore be described as normal.

Ash.—The residue from the moisture estimation is carefully ashed and the ash analysed. The quantity of ash in moêllon made by the pressure method is only a few 100ths of 1 per cent., but in dégras up to 3 per cent. The ash of moêllon consists chiefly of lime, that of dégras, besides sulphates, contains calcium carbonate (from calcium soaps) and sodium carbonate (from sodium soaps). Dégras materials should contain no iron oxide (derived from iron soaps).

Substances insoluble in Petroleum Spirit (Soaps, Leather Fibres, Dirt, etc.).—20 g. of dry dégras are dissolved by gently warming in 150 c.c. of petroleum spirit, filtered through a weighed and previously dried asbestos filter tube, the residue thoroughly washed with petroleum spirit, dried and weighed. The latter consists chiefly of leather fibres, dirt, and soaps. The mineral constituents must be determined by specially incinerating.

Unsaponifiable Matter. — The method of estimation has been described in connection with fish oils (pp. 486).

Oxidised Fatty Acids (Fahrion).—This estimation depends upon the fact that the free oxidised fatty acids are insoluble in petroleum spirit. For the determination, 10 g. of dégras are saponified with constant stirring in a porcelain basin on the water-bath, by the addition of about 7 g. of potassium hydroxide, which have been dissolved previously in about 10 c.c. of water and 50 c.c. of alcohol. When the alcohol has been completely driven off, the contents of the basin are dissolved in about 100 c.c. of hot water, poured into a separating funnel, the soap separated by the addition of a slight excess of dilute sulphuric acid (1 : 4) or hydrochloric acid, and after cooling shaken out carefully for five minutes with petroleum spirit, which should contain no fraction boiling above 70°. When, after several hours' standing, the petroleum spirit has separated clear from the water, the latter is withdrawn from below, when the oxidised fatty acids adhere to the walls of the vessel. The petroleum spirit can then be poured from the upper opening of the separating funnel, free from oxidised fatty acids. The latter are again washed several times with small quantities of petroleum spirit (if wool fat be present, which is mostly indicated by turbidity of the

solution), also with warm petroleum spirit with slight shaking (without inserting the stopper) until all soluble fatty acids are removed. The oxidised fatty acids are then dissolved in a little warm alcohol, and the filtered solution evaporated in a weighed platinum basin on the water-bath, and dried to constant weight at 105°. The soap solution used for the estimation of unsaponifiable matter, after extraction, may also be used for the determination of the oxidised fatty acids.

Mineral Acids.—If the dégras shows a strongly acid reaction, 25 g. are boiled with 200 c.c. of water, allowed to cool, the two layers separated by means of a separating funnel, the nature of the acid (especially sulphuric) determined in an aliquot part of the aqueous layer, and another portion titrated with normal alkali.

Free Fatty Acids.—The acid value is determined as usual, and calculated as oleic acid (taking into consideration the mineral acid if present).

Fats and Oils.—The fatty acids in the petroleum spirit solution, freed from unsaponifiable matter and oxidised fatty acids, are washed with water to remove mineral acids, and the petroleum spirit distilled off. The fatty acids so obtained can be examined further as to saponification value, iodine value, melting point, solidifying point, etc., to obtain information as to the fats contained in the dégras.

Density of Water-free Dégras (Simand).—The dégras is carefully heated to 105° until the water has all been removed, the residue after cooling treated with petroleum spirit, and the solution freed from soaps by shaking with very dilute hydrochloric acid, which is afterwards removed by washing with water. After distilling off the petroleum spirit from the filtered solution the fats of the dégras remain behind. These are quite fluid at ordinary temperatures and only a few samples deposit solid constituents after some time. The specific gravity rapidly increases and the refractive index decreases with the content of oxidised fatty acids. Simand gives the following representative examples :—

	Sp. gr.	Oxidised fatty acids.	Refractive index.	Melting point of fatty acids.	Ash.
		Per cent.			Per cent.
1.	0·9603	16·65	1·474	30°·5 to 31°	0·078
2.	0·9749	18·53	1·480	33°·5 „ 34°	0·025
3.	0·9785	18·39	1·478	34°·5 „ 35°	0·062
4.	0·9915	23·33 *	1·486	34°·0 „ 34°	0·019

* These numbers were obtained from a test in a Bohemian dégras works, and are the highest that Simand ever found.

The oils used in the manufacture of Nos. 2 and 4 had specific gravities of 0·9269 and 0·9294 respectively, and contained 1·18 per cent. and 1·47 per cent. of oxidised fatty acids; the melting points of the

fatty acids were from 31°-31°.5. Eitner has also conducted researches on these lines.[1]

For a number of years artificial dégras has been prepared by the direct oxidation of fish oils (by blowing air into the warm oil, or some other method of oxidation) and subsequent emulsification with water. If these substances are prepared from good raw materials, and if they are sufficiently oxidised and emulsified, they are just as valuable as natural moêllon or dégras. In addition, a large number of products come into commerce, consisting of natural or artificial dégras with the addition of fish oil, tallow, palm and cocoa-nut oil, wool fat, vaseline, mineral and rosin oils, colophonium, and other cheap fats.

An appreciable addition of tallow raises the melting point of the fatty acids, and that of cocoa-nut oil or palm oil raises the saponification value; in normal dégras both (calculated on the moisture-free material) are about the same or very little higher than those of fish oil.

Vaseline, Mineral and Rosin Oils are estimated in the same way as in fish oils (p. 486).

Wool Fat.—For this estimation 5-6 g. of dégras are saponified as above, the fatty acids extracted from the soap solution and treated with ether. The ethereal solution is evaporated in a small weighed flask, the residue boiled under a reflux condenser with one and a half times its quantity of acetic anhydride for one to two hours, water added, and then, to remove the acetic acid, boiled out several times with water. The whole is then dried and the acetylated fatty acids, the cholesteryl acetate, etc., dissolved in fifteen times the quantity of alcohol (75-150 c.c.) on the steam-bath and again cooled. The difficultly soluble cholesteryl acetate which is again almost completely precipitated on cooling, is filtered off, again crystallised twice from fifteen times the quantity of alcohol (to remove the vaseline oil as completely as possible), and then dissolved in ether; the ether is distilled off and the residue weighed. Wool fat yields as a mean of very variable values (9.59-18.71 per cent.) 14.05 per cent. of cholesteryl ester. If the weight of the ester be multiplied by 7, a rough approximation as to the proportion of wool fat present is obtained.

The presence of wool fat is recognisable, according to Simand, by the shiny surface of the solidified fats, or if these do not solidify, by the shiny non-crystalline surface of the fatty acids extracted after saponification. By rubbing some of the oil on the surface of the hand the characteristic smell of wool fat may be recognised.

For the estimation of *Colophonium* (resin), the soap solution derived from the determination of the unsaponifiable matter is decomposed with hydrochloric acid and washed; in this way the mixture of resinous and fatty acids is obtained, in which the rosin acids are determined by

[1] *Gerber*, 1893, 19, 243, 257.

Twitchell's method. This process depends on the conversion of the fatty acids, by the action of hydrochloric acid gas on their alcoholic solution into their ethyl esters, whilst rosin acids remain unaffected by this treatment. The method is described in the section on "Special Methods of Analysis employed in the Oil and Fat Industries," this Vol., p. 195.

According to the regulations of the I.A.L.T.C., the examination of the fats shall proceed according to the following general scheme :—

Moistures.
Mineral matters.
Substances insoluble in petroleum spirit, ash-free (non-fatty matters).
Substances soluble in petroleum spirit $\begin{cases} \text{unsaponifiable matter.} \\ \text{saponifiable matter.} \end{cases}$

In dégras and such materials the proportion of oxidised fatty acids must be determined in addition to the other constituents.

Vaseline Oils and Mineral Oils,[1] which are used in the leather industry mainly as adulterants, should have a density of from 0·88-0·90 at 15°. On cooling to low temperatures (− 10°) for one to two hours they should only become thick, and in no case should deposit any appreciable quantity of solid paraffins ; they must be free from sulphuric acid, which may be estimated by shaking out with warm water in the presence of glass beads. Adulteration with rosin oils can be recognised by the raising of the density and of the refractive index.

Soaps.—Soaps are used in the preparation of the soap stuffings used in the dressing of upper-leathers, and especially in chrome tanning for the preparation of fat-liquors, which are watery fat emulsions made with the assistance of soap and alkali carbonates. A slight free alkali content is not in this case disadvantageous, as the soaps come into contact with the oils, which contain free fatty acids. To obviate precipitation, etc., the soap should be as free as possible from solid fatty acids, and should be prepared from non-drying oils, of which olive, castor, and cold-tested neat's-foot oil are suitable. For the more complete examination of soaps, see the section on "Special Methods employed in the Oil and Fat Industries," this Vol., pp. 188 *et seq.*

V. CONTROL OF WORKING CONDITIONS.

The Estimation of Nitrogen by the Kjehldahl method provides in almost all stages of tanning a very valuable means of works control. In the soaks, limes, and tan liquors the amount of dissolved hide substance, and during tanning and in the finished leather the degree of tannage, is in this way easily determined. According to the researches of von Schroeder and Paessler, the hides which normally come into consideration in leather manufacture, viz., ox, calf, horse, and pig, have in the water-, ash-, and fat-free hide substance a constant nitrogen

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[1] *Cf.* Simand, *Gerber*, 1890, **16**, 193.

content of approximately 17·8 per cent. To estimate the amount of hide substance, the quantity of nitrogen found must therefore be multiplied by 5·62.

According to Paessler, the best method of carrying out the Kjehldahl method is to disintegrate the material by the addition of 15 c.c. of concentrated sulphuric acid and 0·7 g. of mercury. For further details of the method, see the section on "Artificial Manures," Vol. II., pp. 375 et seq. According to the amount of the nitrogen present, 0·5-1 g. of the material is taken for the determination. The disintegration must be continued until the solution is absolutely colourless. To accelerate the process, the use of sulphuric containing 200 g. per litre of phosphoric anhydride is to be recommended.

If it is required to estimate the nitrogen in liquids, it is necessary before disintegration to evaporate to dryness with the addition of a little sulphuric acid to fix the ammonia, and a little ferrous sulphate to destroy nitric acid.

To test for *Dissolved Albuminous Substances in Soak Waters or Lime Liquors* the method of A. Jolles[1] may be applied :—The filtered liquor is treated with clear calcium chloride solution and then acidified, when the albumins come down as a flocculent precipitate. These can then be estimated quantitatively either gravimetrically or by the Kjehldahl method. Eitner[2] has proposed to substitute sodium hypochlorite for calcium chloride. He differentiates the dissolved albuminous materials in lime liquors as :—

(*a*) Soluble hide substance combined with lime.
(*b*) Lime-free soluble hide substance.
(*c*) Hydrolysed hide substance (Peptone).

By precipitation with carbonic acid (*a*), with acetic acid (*b*), and with hypochlorous acid (*c*), fractions may be precipitated and separated.

E. Stiasny[3] estimates the dissolved hide substance in soaks and limes by a method which depends on the titration of equal quantities of the liquor to be tested with and without the addition of formaldehyde; the difference in the quantities required is taken as a measure of the dissolved hide substance present. Sulphides, etc., must previously be removed by the addition of iodine. This method has the advantage of being rapidly executed, but the disadvantage that no absolute values but only proportional figures are obtained.

The action of the lime liquor depends upon its content in caustic lime, ammonia (by decomposition of hide substance), sulphides and enzymes. The estimation of the caustic alkali and ammonia can be performed in one operation, in which the ammonia is distilled over from the clear lime liquor into $N/10$ sulphuric acid and the excess of

[1] Z. Anal. Chem., 1890, 29, 406.   [2] Gerber, 1895. 21, 157, 169.
[3] Collegium, 1908, p. 371 ; 1910. p. 181 ; J. Soc. Chem. Ind., 1908, 27, 1031 ; 1910, 29, 771.

acid titrated back, whilst the residue left in the distillation flask is ti-
trated with $N/10$ acid in the presence of phenolphthalein, and the calcium
hydroxide thus estimated. This distillation should not be pushed too
far, as lime liberates ammonia from the organic matter always present.

Tan Liquors.—For the control of fresh liquors, such as tan liquors,
the barkometer is generally used in practice as a means of determining
their strength and maintaining their constancy. Old and used liquors,
as, for example, the suspender liquors, in which the hides commence the
process, cannot be dealt with in this way owing to the large non-tannin
content which completely vitiates the results. As barkometer, an
ordinary hydrometer, made either of glass or metal, is used, either with
arbitrary degrees or with the divisions of some standard scale, e.g., such
that the distance between each pair of graduations corresponds to 0·001,
sp. gr. (25° barkometer = 1·025 sp. gr.). These latter are described in
England and America as "Barkometer degrees," but Eitner calls them
"degrees Eitner." A definite conclusion as to the relative tannin
strength from the barkometer reading is only possible with fresh
liquors and those made from the same raw materials or mixtures;[1]
with used liquors a comparison is only possible if they have all had
similar treatment (as, for instance, in the successive pits of a series of
handlers or suspenders). With liquors from different tanneries and
different sets of handlers this is usually no longer permissible. Even
with fresh liquors from the same tanning materials the ratio of the tans
to the non-tans varies according to their origin and value, as is shown
by the following results obtained by Paessler.

100 c.c. liquor of sp. gr. 1·014 = 14° barkometer, contain :—

	Tans.	Non-tans.
	g.	g.
Sumac .	1·9	1·4
Pine bark	2·1	1·7
Dividivi	2·2	1·1
Oak bark	2·2	1·2
Oak wood extract .	2·3	1·4
Myrobalans .	2·3	1·0
Valonia .	2·5	0·9
Trillo .	2·5	0·8
Chestnut wood extract .	2·5	1·2
Knoppern	2·5	0·8
Gambier	2·6	1·0
Mimosa bark	2·9	0·6
Quebracho extract (cold soluble) .	3·1	0·6
Mangrove bark	3·4	0·5
Quebracho extract (ordinary)	3·8	0·3
Quebracho wood .	3·9	0·3

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[1] Cf. Paessler, Collegium, 1904, p. 116; J. Soc. Chem. Ind., 1904, **23**, 553. While the indica-
tions of the barkometer are of little value as regards the total tannin present, they give pretty
accurate information of the loss during use, if readings are made before and after an operation.

It is obvious from this Table that a correct valuation of tan liquors can only be made by the direct estimation of the tannin content.

Fresh Liquors, *i.e.* such as are obtained by the extraction of fresh tanning materials with water, do not contain acids produced by fermentation, and are examined in exactly the same manner as extracts. The proportional quantities prescribed for the examination of tanning materials and extracts require consideration.

Used Tanning Liquors, *i.e.* those containing free acid due to fermentation,[1] or the addition of organic or mineral acids, are in all cases to be analysed by the I.A.L.T.C. official hide-powder shake method, as the acids, which are partly taken up by the hide powder, have a smaller effect on the results obtained by this method than on those obtained by the filter method.

B. Weiss[2] recommends that the liquor should be examined by gravimetric methods, but that the quantity of acid should be estimated in the residues (total solids and non-tans) and allowed for in calculation, acid-free total solids minus acid-free non-tans giving the actual tanning substances. In this way the estimation as tannin of acid absorbed by the hide powder would be prevented.

Besides tans and non-tans, the total acid, the volatile acids, and the non-volatile acids are also of importance and must be estimated. The volatile acids derived from fermentation are, as Wladika[3] has shown, mostly acetic, and the non-volatile acids chiefly lactic; but this varies considerably in different yards and with different materials.

Acidity (*Total Acids*).—The following methods are in use for this estimation :—

Procter's Method.[4]—This simple method consists in running clear standardised lime water from a burette into the clear filtered liquor until a permanent cloudiness of calcium tannate is produced. If the liquors are too dark they must be diluted. The carbonic acid, which is present in most liquors which are not too old, is, of course, in so far as it is not removed by shaking, partially estimated by this method. It can, however, be removed before titration by adding common salt and shaking vigorously.

Koch's Method,[5] improved by Paessler and Spanjer.[6]—In this method 25 c.c. of the clear, filtered liquor are measured into an Erlenmeyer flask and precipitated with 25 c.c. of gelatin solution (5-6 g. purest gelatin dissolved in 1 litre of hot water, and the solution filtered after

[1] *Cf.* F. Andreasch, *Gerber*, 1895-97, vols. 21-23 ; *J. Soc. Chem. Ind.*, 1896, 15, 916; 1897, 16, 52, 248, 340, 620, 740, 925, 1025.

[2] *Gerber*, 1895, 21, 63.   [3] *Ibid.*, 1890, 16, 3, 15, 28, 61.

[4] *Proc. Newcastle-on-Tyne Chem. Soc.*, 27th March 1879.

[5] *Dingl. polyt. J.*, 1887, 264, 395 ; 265, 33 ; 267, 459, 513 ; 1888, 269.

[6] *Gerber Zeit.*, 1899, 32, Nos. 76 and 77 ; 1900, Nos. 45, 50-53, and 55 ; *Collegium*, 1903, p. 10 ; *J. Soc. Chem. Ind.*, 1899, 18, 773, 927.

cooling). The precipitate must come down quickly and thoroughly in the flocculent form; if this be not the case, a more dilute gelatin solution must be used (with weak tan liquors a gelatin solution of 2 g. per litre usually suffices). The unfiltered solution is then titrated with baryta water or lime water of known strength, and the end-point recognised by spotting on litmus or azo-litmin paper. The acidity of the gelatin solution must be determined and subtracted from the alkali required. The total acidity is calculated as acetic acid per 100 c.c. of liquor.

A. Hoppenstedt[1] has recommended the precipitation of the tannin with quinine solution, and the subsequent titration of the filtrate with $N/10$ alkali. According to C. Bennett and C. D. Wilkinson[2] the method is so full of difficulties as to be valueless.[3]

Estimation of Volatile and Non-volatile Acids.—For this estimation, 100 c.c. of the liquor to be examined are distilled in steam with a condenser attached, until there are 300 c.c. of distillate and the liquor is reduced to about 20 c.c. The acidity of an aliquot portion of the distillate is estimated by titration in the presence of phenolphthalein and calculated as acetic acid. If the volatile acidity be subtracted from the total acidity, the non-volatile is obtained and calculated as lactic acid by multiplying by 1.5. The latter value can be determined independently by cooling the residue in the distillation flask, making up to 100 c.c., and determining the acidity of an aliquot portion in the same manner as the total acidity, and calculating as lactic acid.

It is obvious that in such mixtures of weak acids and their salts, the amount of acid estimated will largely depend on the indicator used, and no useful comparison can be made between titrations made with different indicators or under different conditions. (Procter.)

Spent Tanning Materials.—In order to determine the extent to which tanning materials are exhausted, they are examined after use as to the tannin they still contain. To estimate this tannin the material is dried, ground, and then examined exactly in the same way as fresh materials, except that a greater weight is taken and that, after extraction, the solution must be brought to the required strength. The results are given on the air-dry weight of the material. In order to compare the tannin residue in extracted materials with that in fresh, the former must be recalculated to the original weight of the latter by multiplying the tanning content by the percentage of insoluble matter found in the original material, and dividing by the percentage of insoluble matter found in the spent material, the insolubles being

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[1] *Collegium*, 1907, p. 77 ; *J. Soc. Chem. Ind.*, 1907, **26**, 331.
[2] *J. Soc. Chem. Ind.*, 1907, **26**, 1186.
[3] *Cf.* also *Collegium*, 1907, p. 77 ; 1910, pp. 298, 406, 410 ; 1911, pp. 150, 219, 225, 233, 432.

unaffected by the extraction. For further details, see section on "Vegetable Tanning Materials," this Vol., pp. 458 *et seq.*

VI. THE EXAMINATION OF LEATHER.

Sampling.—To obtain a true sample of a parcel, pieces must be cut from the butt, bellies, and shoulders of each of several hides. The single parts of the hide give essentially different results, by reason of their different constitution and texture. The samples taken must be cut up into small pieces and ground in a mill to a uniform woolly powder. If, as in the case of heavily stuffed leathers, grinding is not permissible, the leather must be cut up into the smallest possible pieces.

(a) Vegetable Tanned Leather.

Moisture.—For this estimation, 10 g. of the finely ground leather are dried at 100°-105° to constant weight. These results, if it is not expressly stated otherwise, should be calculated, according to the recommendations of von Schroeder,[1] to the average water content, which happens to be the yearly mean of that kind of leather. These yearly means have been established by von Schroeder; the average water content of the unstuffed leathers (sole, light and inner-sole leathers) is about 18 per cent., and that of stuffed leathers (belting, various kinds of harness leathers, upper leathers) is dependent on the fatty content of the leather, and can be calculated according to the following formula :—

$$W = \frac{1800\,(100 - F)}{8200 + 18\,(100 - F)},$$

where W is the average water content and F the fat content of the dry leather. To judge the moisture of air-dry leather which has been stored normally the following rule may be used :—If the average moisture content of unstuffed vegetable tanned leather is taken as 18 per cent., then in the dry and warm season this will sink to 15.5 per cent.; in the moist, cold season it will rise as high as 20.5 per cent.; so that the variation in the course of the year is about ±2.5 per cent. For stuffed leathers the average water content is dependent on the fat content of the dry leather ; generally speaking, the variations throughout the year are somewhat smaller, being about ±2 per cent. In leathers which have been dried at high temperatures, as in the Austrian *Terzen*, the moisture is generally slightly lower, as this leather, even after lengthy storing, does not reach the water content of other leathers.

[1] *Dingl. polyt. J.*, 1894, 293 ; *J. Soc. Chem. Ind.*, 1895, 14, 587.

Obviously the average moisture of a leather will vary widely with the season, the climate, and the mode of drying. In England, 15 per cent. is nearer the average, as heat is almost always used. It is necessary, therefore, to give the actual water found, even if a calculation to 15 per cent. or to dry matter is added. (Procter.)

Estimation of Mineral Matter (Ash).—10 g. of the leather are carefully and completely incinerated at a low red heat in a platinum basin; the addition of ammonium nitrate is sometimes necessary. The mineral content of a normal leather (on the air-dry weight) varies between 0·25-1·6 per cent., and with sweated leathers is naturally lower than with limed leathers. A content greater than 1·2 per cent. usually signifies either bad workmanship in the cleansing processes (insufficient deliming), or the use of tanning extracts rich in mineral matters (sulphited extracts), or the addition of magnesia salts to the tan liquors to accelerate tanning, or the treatment of the leather with mineral matters (alumina, etc.); and one of over 2 per cent. usually signifies the weighting of the leather therewith, though in sole leather a somewhat higher limit must be allowed. In cases of weighting this limit is usually appreciably overstepped, so that sometimes a mineral matter content of over 20 per cent. is found. In such cases a qualitative analysis of the ash will indicate the nature of the material, which can then be confirmed by the quantitative estimation. Among mineral weighting substances are the following:—Barium chloride, barium sulphate (formed in leather by double decomposition or mechanically applied), and less frequently, common salt, magnesium and sodium sulphates, lead salts (nitrate or acetate).

Magnesium sulphate, and sometimes sodium sulphate, in conjunction with glucose are among the commonest weighting materials in present use, both for leather and textiles; and it must be remembered that the weight actually obtained is higher than that of the dry mineral ash by the water of crystallisation. (Procter.)

Estimation of the Fat.—20 g. of leather are extracted in a Soxhlet apparatus for three to four hours with carbon bisulphide and the quantity of fat then determined in the usual manner. The estimation of fat must also be made on the unstuffed leathers, as these contain natural fats, so-called skin-fats. The fatty content of unstuffed leathers varies between 0·2 and 1·2 per cent.; in light-sole leather, which is usually lightly oiled (with linseed or fish oil), it sometimes rises to 3 per cent. Sheep-skins have generally a high natural fatty content.

Estimation of the Loss on Washing (Auswaschverlust) and of the content of Extractable Tans and Non-Tans.—Every vegetable tanned leather contains a certain quantity of substances which can be washed out by water at ordinary temperatures, and which are described collectively as "loss on washing." For their estimation, 20 g. of the

powdered leather, freed from carbon bisulphide, are placed in a Koch extractor (see under "Vegetable Tanning Materials," p. 456) with or without a layer of sand ; after soaking in water for about twelve hours, it is extracted at the ordinary temperature to a total volume of 1 litre within one and a half to two hours, and the infusion filtered. Then 200 c.c. of this solution (derived from 4 g. of leather) are evaporated to dryness in a platinum basin, and the residue dried to constant weight, weighed, incinerated, and again weighed ; the total quantity of organic soluble matter is thus obtained. Weighting with soluble mineral salts, barium chloride, sodium chloride, etc., is also estimated by this means.

Methods and temperatures of extraction are at present somewhat variable, and it is very desirable that some definite decision on the point should be reached.

For the estimation of non-tans, 500 c.c. of the solution are evaporated to 125 c.c., which still represents 10 g. leather, the tannin removed therefrom by hide powder in the usual manner (see p. 472), and 50 c.c. of the filtrate evaporated to dryness and the residue dried to constant weight and weighed as non-tans ; the residue is finally incinerated, and the amount of organic non-tans so obtained. The tannin is obtained by subtracting the ash-free non-tans from the ash-free loss on washings.

The organic "loss on washing" of the various kinds of leather differs widely, and varies in normal unweighted leathers (air-dry), as follows :—

	Per cent.
In sole and light-sole leathers from . .	3 to 20
In belting leathers from	3 ,, 10
In upper leathers	3 ,, 10

Leathers tanned in strong liquors give a high "loss on washing"; from this basis conclusions may frequently be drawn as to the nature of the tannage which any piece of leather has undergone. The highest "loss on washing" is found in North German sole leathers, English light-sole leathers, and Austrian Knoppern- and Valonia-terzen. The amount of tans and non-tans in the "washings" serves also for the detection and estimation of weighting with organic materials, such as sugar, glycerin, etc. (The weighting materials most frequently used are glucose and the other starch sugars.) In unweighted leathers the amount of the tans is at least as great as that of the non-tans, so that if the latter exceeds the former weighting must be suspected, and qualitative tests and a quantitative determination made. (For further details see the estimation of sugar, p. 502.)

Estimation of Hide Substance and Combined Tannin.—For this determination use is made of the fact that hide substance contains nitrogen while the other substances present do not. The percentage of hide substance can therefore be calculated from the nitrogen content of

the leather; the quantity of combined tannin is then 100 minus the sum of the other constituents, viz., water, mineral matters, fat, "washings," and hide substance.

According to von Schroeder and Paessler,[1] the nitrogen content of the moisture, ash, and fat-free hide has the following values:—

17·8 per cent. in cow (calf, kips), horse, and pig skins; 1 per cent. nitrogen equivalent to 5·62 per cent. hide substance.

17·4 per cent. in goat, deer, and buck skins; 1 per cent. nitrogen equivalent to 5·75 per cent. hide substance.

17·1 per cent. in sheep skins; 1 per cent. nitrogen equivalent to 5·85 per cent. hide substance.

The nitrogen estimation is carried out according to the Kjehldahl method with 0·6 g. of powdered leather (see p. 493).

The results of the analysis are arranged as follows:—

Moisture.
Mineral matters.
Fat.
Organic "loss on washing" $\begin{cases} \text{Tans.} \\ \text{Non-tans.} \end{cases}$
Leather substance $\begin{cases} \text{Tannin.} \\ \text{Hide substance.} \end{cases}$

To von Schroeder is also due the conceptions of "leather yield" (R) and "degree of tannage" (D), which provide much information as to extent and nature of the tannage, which is otherwise only obtainable from the percentage figures.

The "leather yield" (R) of a leather represents the number of parts of air-dry vegetable tanned leather which have been derived from 100 parts of hide substance.

Example: A leather in the dry condition contains 45·0 per cent. of hide substance:—

$$R : 100 :: 100 : 45.$$

$$\text{then, } R = \frac{100 \times 100}{45} = 222 \cdot 2.$$

The "degree of tannage" represents the number of parts of tannin fixed by 100 parts of hide substance.

Example: A leather in the dry condition contains 45 per cent. of hide substance and 30 per cent. of tannin (which cannot be washed out):—

$$D : 100 :: 30 : 45.$$

$$\text{then, } D = \frac{100 \times 30}{45} = 66 \cdot 7.$$

According to von Schroeder and Paessler, D in most leathers is essentially below 100, although with very thorough tannings with

[1] *Dingl. polyt. J.*, 1893, **287**, Parts 11, 12, 13; *Collegium*, 1905, p. 340.

strong liquors leathers are produced which reach and even exceed this limit. *Very much* higher figures are reached by English sole-leather tanners. (Procter.)

Estimation of Sugar.—The sugar content is only estimated when the loss in washing is very considerable, and when the non-tans exceed the tans to such an extent that weighting with sugar is suspected. Small quantities of sugars, derived from the tan liquors, can be found in most leathers; according to von Schroeder, the average sugar content of unweighted leathers is about 0·25 per cent, and may rise as high as 2·0 per cent.

Leather tanned largely with myrobalans may somewhat exceed this figure. (Procter.)

In avowedly weighted leathers it may be anything from 2-16 and more per cent.

For the estimation of sugar the following solutions are required :—

1. *Copper Sulphate Solution*, containing 69·2 g. of purest copper sulphate per litre.

2. *An Alkaline Solution of Rochelle Salt*, containing 346 g. of Rochelle salt and 250 g. of potassium hydroxide per litre.

3. *Lead Acetate.* 300 g. of lead acetate are thoroughly ground up with 100 g. of pure litharge and about 50 c.c. of water, and heated on the water-bath until the paste has become white, further small quantities of water being added if necessary. The mass is transferred to a litre flask, cooled, filled up to the mark, and after standing for some time, filtered.

4. *Sodium Sulphate Solution.* It is essential that this solution should be of equivalent strength to the lead acetate solution.

To carry out the sugar estimation, 400 c.c. of the extracted solution (derived from the "washings") are evaporated to 100 c.c., which is consequently equivalent to 8 g. of leather. These 100 c.c. are transferred to a dry vessel, the tannin precipitated with 15 c.c. of basic lead acetate solution, and allowed to stand, with frequent shaking, for fifteen minutes, and then filtered through a dry filter into a dry flask (the filtrate must be free from tannin). To 50 c.c. of the filtrate (representing $\frac{8 \times 50}{110} = 3.637$ g. of leather) are added 5 c.c. of the sodium sulphate solution, and the precipitate, after it has thoroughly settled, filtered through a dry filter. Of this filtrate 40 c.c. (representing $\frac{3.637 \times 40}{55} = 2.645$ g. of leather) are used for the sugar estimation as follows :—30 c.c. of the copper sulphate solution, 30 c.c. of the alkaline Rochelle salt solution, and 45 c.c. of distilled water are poured into a 200 c.c. beaker and heated over a small naked flame to boiling. The beaker is then placed on a boiling water-bath ready to hand, and the

40 c.c. of sugar solution added whilst stirring. The beaker is allowed to remain on the water-bath for exactly thirty minutes after adding the sugar solution. The precipitated copper oxide is filtered through a weighed asbestos filter with the help of the pump, then washed with warm water and, to promote rapid drying, with small quantities of alcohol and ether. The filter is gently ignited for a short time to remove traces of organic matter precipitated with the copper oxide, and then reduced in a current of hydrogen, allowed to cool in the same, and quickly weighed. The amount of glucose originally present can be determined by multiplying the weight of copper found by 0·469. In exact analyses the use of this latter factor is inadmissible, as it is merely an average figure, and the quantity of sugar equal to the weight of copper found should be obtained from the special Tables which have been worked out for this purpose. (See Section on " Sugar," p. 557.)

The total volume of alkaline copper solution and the solutions added to it should always be 145 c.c.

The above method determines glucose and allied substances but not cane sugar, or the dextrinous matters found in commercial starch sugars and molasses. Leather is never weighted with pure glucose, owing to the expense of such a method, but with commercial starch sugars, starch syrup or molasses. To estimate these materials when present in addition to starch sugar, the following method may be employed :—40 c.c. (representing 2·645 g. of leather) which have been freed from tannin and lead, as mentioned above, are heated on a boiling water-bath for half an hour with 10 c.c. of dilute sulphuric acid (1 : 5) to invert the cane sugar; after cooling, the solution is neutralised with sodium hydroxide, made up to 100 c.c., and 50 c.c. of this solution (representing 1·323 g. of leather) are submitted to a second sugar estimation, which is carried out in exactly the same way as the first with the same precautions as to half an hour's boiling. Of the amount of copper obtained, one half (the other half being represented by the previous estimation) represents the " invert sugar," the amount of which can be found by multiplying this value by 0·95.

To assist in the judgment of many leathers, especially those which have been limed or treated with sulphuric acid, it is in many cases of interest to determine the contained sulphuric acid (SO_3) and lime (CaO), especially with a view of ascertaining whether the skin has been properly delimed.

Estimation of Sulphuric Acid and of Lime.—For this determination 20·0 g. of the powdered leather are brought into a litre flask, with 750 c.c. of approximately 1 per cent. hydrochloric acid (30 c.c. of hydrochloric acid of sp. gr. 1·125 and 720 c.c. of water), and allowed to stand for twenty-four hours at 30°-40°. After cooling, the solution is at once made up to 1 litre and filtered. For the sulphuric acid estima-

tion 250 c.c. of the filtrate are evaporated to dryness, the residue moistened with 25 c.c. of 10 per cent. sodium carbonate solution (free from sulphuric acid), evaporated to dryness, carefully incinerated, and dissolved in just sufficient dilute hydrochloric acid to render the liquid faintly acid. The estimation of the sulphate is then carried out as usual.

For the estimation of the lime 500 c.c. of the filtrate are evaporated to dryness, the residue incinerated and dissolved in dilute hydrochloric acid. After precipitating the iron, etc., the calcium is determined in the usual manner.

The sulphuric acid determined as above represents neither the total content of the leather in SO_3 nor the free sulphuric acid present. In spite of this fact the figure so obtained is of value in judging a leather by giving some idea as to the extent to which sulphuric acid has been used in its manufacture. If it is required to know the true sulphuric content, the estimation can best be carried out by the Balland-Maljean method as improved by Paessler and Sluyter,[1] and by Arnoldi.[2]

This method has been much criticised, and has several sources of error, but no unimpeachable method is known, or perhaps possible. (Procter.)

According to this method the total sulphates and the combined sulphates are determined in the leather, and the difference between them is the free sulphuric acid. 5 g. of the leather are moistened with a 10 per cent. sodium carbonate solution (free from sulphuric acid) and a little potassium nitrate, and, after drying at a moderate temperature, incinerated as completely as possible over a spirit lamp or, better still, in an electric oven. Brunck recommends the use of cobalt oxide as an oxygen carrier during incineration; during the moistening of the leather with the sodium carbonate solution, 1·5-1·8 g. of cobalt oxide are thoroughly mixed in with a clean platinum wire and then the above method of procedure continued. The ash is dissolved by the addition of a little bromine water, and the solution rendered faintly acid with hydrochloric acid. The sulphuric acid is estimated in the filtrate by the usual method (total sulphuric acid). A further 10 g. of leather are incinerated as above, but without the addition of sodium carbonate, and the sulphuric acid determined in the residue in the same manner (combined sulphuric acid). The difference between the two values cannot yet be taken as the free sulphuric acid; it must be remembered that in the estimation of total sulphates the amount of sulphur originally contained in the hide substance has been included. According to Paessler and Sluyter, the error introduced in this manner with a fat-free leather containing 18 per cent. water is about 0·14 per cent.

[1] *Gerber Zeit.*, 1901, Nos. 66 and 69.   [2] *Collegium*, 1908, p. 358.

(reckoned as SO_3), rising to 0·17 per cent. on the dry leather substance. In order, therefore, to obtain the free sulphuric acid content, 0·14 per cent. should be subtracted from the difference obtained (total sulphuric acid minus combined sulphuric acid).

In this method it is of importance to know whether the leather under examination contains aluminium, chromium, or iron sulphate. If this should be the case, the material in the estimation of fixed sulphuric acid should be ignited until the sulphuric acid contained in these salts is completely removed; in addition, an estimation of the oxides of the elements must be carried out. The amount of sulphuric acid necessary to combine with these bases must then be subtracted from the amount of free sulphuric acid estimated as above.[1]

A. Wuensch[2] estimates the total sulphuric acid after disintegration of the leather by means of fuming nitric acid.

According to L. Meunier,[3] appreciable quantities of sulphur are volatilised in the Balland-Maljean method, as described above, which would otherwise be estimated. He recommends that the leather should be moistened before incineration with a 10 per cent. solution of potassium hydroxide and sodium nitrate; 0·20 per cent SO_3 must then be subtracted as the sulphur due to the hide.

Meunier[4] recommends that the incineration of the leather in the estimation of sulphuric acid should take place in a Mahler bomb in an atmosphere of oxygen under 30 atmospheres' pressure.

A simpler and more rapid method for the determination of sulphuric acid is that of Procter and A. Searle.[5] From 2-3 g. of the leather are moistened in a platinum basin or crucible with 25 c.c. of $N/10$ sodium carbonate solution, evaporated to dryness, and the mixture thoroughly carbonised at a gentle heat; the whole of the organic sulphur is thus removed as volatile compounds. The residue is pulverised with a glass rod, extracted with boiling water, the solution filtered through a small ash-free filter paper, which is dried, returned to the crucible, and the whole ignited till all, or nearly all, the carbon has disappeared. The crucible is then allowed to cool, the ash treated with 25 c.c. of $N/10$ hydrochloric acid to dissolve any calcium carbonate present, the whole washed into a beaker with the filtrate of the charred mass, methyl orange added, and the liquid titrated with $N/10$ sodium carbonate. The total volume of standard alkali used, both before and after ignition, less the volume of standard acid employed, gives the content of sulphuric acid.

[1] Sulphuric acid may also be introduced by sulphonated tanning materials, sulphated extracts, and sulphonated dyes, which will be estimated as if free. (Procter.)

[2] *Wissenschaft. tech. Beilage des Ledermarkts*, 1901, p. 141.

[3] *Collegium*, 1906, p. 15.

[4] *Ibid.*, 1906, p. 296; *J. Soc. Chem. Ind.*, 1906, 25, 913.

[5] *Leather Trades Review*, 1901, 34, 19; *J. Soc. Chem. Ind.*, 1901, 20, 287.

Estimation of the Specific Gravity.—A weighed strip of the sample, 25-30 cm. long and 1-1·5 cm. wide, is placed in a glass tube, which is graduated to 0·5 c.c. and filled to the mark with mercury, the strip being pushed under the surface of the mercury with a needle in such a way that the volume of the leather can be determined to 0·25 c.c. by the amount of mercury it displaces. The specific gravity is then calculated in the usual manner.

Another method, which must of necessity be used with all soft leathers, consists in cutting an exactly square piece of the leather, weighing, and measuring to 0·01 mm. with an accurately graduated micrometer with a vernier attachment, in all dimensions. The volume is then calculated, and from this and the weight, the specific gravity. If the leather is to be calculated to its mean percentage of water, the moisture content of the leather must be determined simultaneously.

Nature of the Tannage.—It is impossible to determine with any certainty by means of chemical reactions with what tannins the leather has been treated. The practical tests are dependent on external characteristics, such as colour, cut, etc., but considerable advances have recently been made by Stiasny and others.

According to Procter, the use of pine bark in tanning may be detected by dipping the leather in a concentrated solution of stannous chloride and hydrochloric acid, which takes a deep pinkish-red colour. A few drops of the infusion of a leather tanned with valonia turn a magnificent purple-red colour on the addition of a crystal of sodium sulphite.

Tannin Penetration Test (Acetic Acid Test).—Every leather should be tanned through as completely and as evenly as possible. For the examination a piece of the leather is cut from the strongest part, viz., the tail end of the butt, and the cross section closely examined. A sensitive method of testing is the acetic acid test, the leather being cut from the aforesaid part. This piece is then cut up into smaller pieces, 1·5 mm. wide and about 4 cm. long, which can best be accomplished by a machine specially constructed for this purpose, a microtome leather cutter.[1] These strips are placed for exactly two hours in 30 per cent. acetic acid (sp. gr. 1·0412). Leather which is thoroughly tanned through does not change, swells very little, colours the acetic acid brownish, and appears dark against the light, or in full thickness brownish-red. Insufficiently tanned leather swells greatly, and exhibits against the light transparent waxy yellow strips in the middle.

Test of Strength.—Several appliances have been suggested for the purpose of testing leathers as to breaking strain (important in belting

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[1] Supplied by Messner, Freiberg.

and harness leathers), resistance to friction (sole leather) and to cracking (upper leather). Only those for the estimation of the breaking strain, which also serve for stretching tests, are used in practice. The same appliances, as for textiles, ropes, metals, etc., can be used for this purpose. Fecken-Kirfel in Aix-la-chapelle has a similar machine specially for testing leather. Of two belting leathers with the same breaking strain, the better is that with the less stretch. The breaking strain for a good belting leather should be at least 3 kg. per square millimetre. An increase in the content of the water or of the fat generally raises the breaking strain.

It is very important that the pieces to be tested should always be taken from the same places in the hide. Paessler[1] has carried out extensive researches on this matter.

Water Absorption Test.—This test is of value in the examination of sole leathers; the better such a leather is the less water it should absorb on immersion. To carry out the test a piece of leather of 20 g. weight (the moisture content must be determined simultaneously on another piece) is placed in a flat-bottomed basin and covered with water; after some time the piece is again weighed and again placed in water, and the process continued until the maximum absorption of water is obtained. By careful observation of the method given any appreciable extraction which would affect the result can be avoided. It is absolutely necessary that the water-absorption should refer to a definite percentage of original water in the leather (according to von Schroeder the best is one of 18 per cent.); only then are comparisons admissible.

(b) Chamois Leather.

Chamois leather[2] should have a soft and cloth-like feel, and a certain amount of toughness.

(c) Chrome Leather.

For the last fifteen years leather tanned with chrome combinations has been of great importance, especially for technical and fancy purposes, where it finds innumerable uses.

Estimation of Moisture.—This is determined in 5 g. of the leather in exactly the same manner as with vegetable tanned stock.

Estimation of Mineral Matter.—2 g. of the leather are heated in a platinum crucible until the organic material is completely incinerated (as in the ash determination of vegetable tanned leather). The mineral

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[1] *Collegium,* 1909, p. 45 ; *J. Soc. Chem. Ind.,* 1909, 28, 615.
[2] *Cf.* von Schroeder and Paessler, *Dingl. polyt. J.,* 1895, 295, 9 ; *J. Soc Chem. Ind.,* 1895, 14, 759.

acids united with chromium, aluminium, and the iron oxides are not estimated in this way, as they are driven off during the ignition.

Estimation of Chromic Oxide (Cr_2O_3).—The residue derived from the ignition is thoroughly mixed in a platinum crucible with a mixture of 60 parts of sodium carbonate, 20 parts of potassium carbonate, and 4 parts of potassium chlorate, and gently heated in the yellow flame of a blow-pipe, then for fifteen to twenty minutes with the blast, adding once or twice a small quantity of the above mixture. This mixture is apt to attack the crucible. The ash can be completely oxidised by intimately mixing with equal parts of magnesia and sodium carbonate, and igniting for twenty minutes over a Méker burner, with occasional stirring. A mixture of sodium carbonate and sodium peroxide is also efficient, and after acidification excess of hydrogen peroxide can be removed by boiling. It is impossible to melt the contents sufficiently in a porcelain crucible. The cooled melt is dissolved in hot water and the solution filtered to remove insoluble constituents. The clear filtrate, in which the chromium is present as chromate, is diluted with water to 150 c.c., 5-10 c.c. of concentrated hydrochloric acid and 10 c.c. of 10 per cent potassium iodide solution added, and the whole titrated with thiosulphate solution (exactly as in the titration for the determination of the iodine value of fats). 1 g. of anhydrous thiosulphate corresponds to 0·1603 g. Cr_2O_3.

Estimation of Alumina.—If the leather contains alumina, 3 g. are treated with fusion mixture as above. The melt is dissolved in hot water and the filtrate of this solution made up to 250 c.c. The chromic acid in 100 c.c. of the latter is reduced by the addition of hydrochloric acid and alcohol with continuous boiling, and the chromium and aluminium oxides precipitated from this solution with ammonia and treated in the usual manner, to be weighed finally as $Cr_2O_3 + Al_2O_3$. In a further 100 c.c. of the solution the chromium oxide is estimated, as described above, by titration with $N/10$ thiosulphate solution; the amount of alumina (Al_2O_3) is calculated from the difference. The oxides of chromium and aluminium are usually present in chrome leather in the form of basic sulphates or chlorides.

Estimation of Sulphuric Acid (SO_3) and of Alkalis.—For this estimation 5 g. of leather, extracted with carbon bisulphide to remove fat and sulphur, are dissolved in 50 c.c. of fuming nitric acid. This is accomplished at ordinary temperatures in twelve to twenty-four hours, but this time may be greatly reduced by gently warming. When the leather has in this way dissolved to form a green liquid, the nitric acid is driven off by repeated evaporation with water. The residue is dissolved in water, made up to 500 c.c. and, if necessary, filtered. The sulphuric acid is determined in 200 c.c. of this solution by precipitation in the usual manner with barium chloride. From

the amount of SO_3 found, 0·005 per cent. SO_3 must be subtracted for every 1 per cent. of hide substance in the leather, as · in this method the sulphur·of the hide substance is converted into sulphuric acid:

The alkalis are determined in another 200 c.c. of the solution. For this purpose the solution is evaporated to dryness, gently ignited to destroy organic matter, and the residue extracted with a very dilute solution of hydrochloric acid. From this solution chromic oxide, alumina, iron, and calcium oxides are precipitated by ammonia and ammonium carbonate; the filtrate is evaporated to dryness with the addition of a few cubic centimetres of dilute sulphuric acid, and the residue gently ignited to remove ammonium salts, etc. The alkalis are then weighed as sulphates. If it is required to separate potassium and sodium salts, which are both usually present in chrome leather, the separation can be carried out in the·usual manner.

Estimation of Chlorides.—3-4 g. of the leather are soaked in 25 c.c. of a 10 per cent. sodium carbonate solution (free from chlorine), dried, .and then carefully incinerated, which is best accomplished in a muffle furnace or an electric oven. The ash is completely extracted with water and the chloride in the filtrate or in an aliquot part (the solution to be titrated must be exactly neutralised with nitric acid) titrated with $N/10$ silver nitrate solution, using a neutral potassium chromate solution (not more than 3 drops of a 10 per cent. solution) as indicator.

Estimation of Fat and Free Sulphur.—To estimate the fat, 20 g. of the leather are extracted in exactly the same manner as vegetable tanned leather with carbon bisulphide (free from free sulphur); from this solution the solvent is distilled off, so that the fat remains behind and can be weighed. If the leather contains free sulphur, which is usually the case with two-bath leathers, but may also occur in those of the one-bath, it goes over with the fat. In such cases the sulphur must be estimated and subtracted from the fat. For this purpose the fat is again dissolved in carbon bisulphide, the solution transferred without loss to a platinum basin, the solvent completely evaporated off, and the residue oxidised with red, fuming nitric acid. The resulting solution is evaporated on the water-bath to remove the nitric acid, sodium carbonate solution added, and the whole evaporated to dryness. The residue is carefully ignited to free it from organic materials, extracted with dilute hydrochloric acid and bromine water, and the sulphuric acid precipitated in this solution in the usual manner with barium chloride. The quantity of barium sulphate found is multiplied by 0·135 to give the original quantity of sulphur.

Estimation of Hide Substance.—This is carried out in exactly the same manner as with vegetable tanned leathers. Owing to the higher

content of chrome leather in hide substance, only 0·5 g. of leather should be taken for the determination.

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INK

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English translation revised by C. AINSWORTH MITCHELL, B.A.

A. GENERAL SURVEY.

INK may be defined as a liquid medium for producing writing or other marks upon paper, textile fabrics, glass, metal, or other substances.

Since the raw materials employed in the manufacture of ink also find an. extended use in other branches of chemical industry, it is unnecessary to describe here methods for their examination, and for this purpose the reader may be referred to other Sections of this work.

Moreover, in dealing with so many different kinds of products it is only possible to give a general outline of the methods of manufacture—the more so since many of the processes are jealously guarded as trade secrets.

Before describing the methods of testing various inks, it is advisable to make a general survey over the whole field, dealing chiefly with those of commercial importance and only incidentally with products which are little more than scientific toys.

Commercial inks may be classified into the following main groups, some of which, as is obvious, overlap each other :—

1. Black writing inks, including iron-gall, logwood, and aniline inks.
2. Copying inks.
3. Coloured writing inks.
4. Drawing inks.
5. Printing and lithographic inks.
6. Ticket and stencilling inks.
7. Marking inks.
8. Typewriting inks.
9. Inks for metal, glass, and the like.
10. Sympathetic inks.

They may also be classified in accordance with the character of the pigment, into :—

1. Inks with a pigment in suspension (e.g. printing inks, liquid Indian inks, and marking inks).

2. Inks with the pigment in solution, as in the case of writing, copying, and most typing inks.

Some inks, notably the modern "blue-black" inks, contain a "provisional colouring matter," usually an aniline dyestuff, which is introduced to render the writing sufficiently dark pending the formation of the final black pigment of iron tannate.

In the case of many of the inks included in the above classification, the tests must be based upon their suitability for the special purposes for which they are intended, rather than upon their agreeing with a definite chemical formula, although in some instances the latter is by no means negligible.

B. DESCRIPTION OF DIFFERENT CLASSES OF INK.

I. BLACK WRITING INKS.

The earliest writing inks probably consisted of lamp black suspended in an aqueous solution of glue, and were very similar to the liquid Indian inks of to-day; and it was not until the Christian era was well advanced that iron-gall inks gradually displaced the earlier carbon inks.

Even then, the inks were of a different character from the modern iron-gall inks, since they were made to undergo more or less oxidation before bottling, so as to produce a certain proportion of an insoluble iron tannate, which, remaining suspended within the liquid, caused the writing to appear black immediately.

About the beginning of the last century it was discovered that, as a rule, unoxidised inks gave more permanent writing the formation of the insoluble black iron tannate then taking place within the fibres of the paper, instead of being deposited ready-formed upon the surface.

The older form of iron-gall ink, however, still met with a limited sale under the name of "Japan ink," an example of which is given in the subjoined Table (p. 517).

The provisional colouring matters which are added to prevent the writing appearing too pale when first applied to the paper, include indigo, alizarin, logwood, and aniline dyestuffs. Upon their nature and proportion in relation to the other ingredients of the ink are based methods of distinguishing between different inks in handwriting.

Normal Inks.

This is the name applied in Germany to such writing inks as answer the requirements of the standards fixed by an Imperial Statute of 1st August 1888 (*Grundsätze für amtliche Tintenprüfung*).

Official Classification of Writing Inks.—According to these standards, which are based upon a quantitative determination of the

gallotannic and gallic acids by the method described in Hinrichsen's "*Die Untersuchung von Eisengallustinten*," and upon the methods described in Schluttig and Neumann's "*Die Eisengallustinten*," writing inks are officially classified in Germany into the two following classes:—

Class I. Iron-gall inks, which give black writing when dry, and contain at least 30 g. of gallotannic and gallic acid (derived wholly from galls) and 4 g. of metallic iron per litre.

Class II. Inks which give black writing, which when dried for eight days cannot be removed by alcohol and water. The ink must also flow freely and not be sticky when dry.

Inks of Class I. are suitable for documentary purposes; those of Class II. for writing where less permanency is required.

In Hinrichsen's method of determining gallotannic and gallic acids, the ink is treated with hydrochloric acid and repeatedly shaken with ethyl acetate in Rothe's extraction apparatus (see section on "Iron," Vol. II., p. 9). The united extracts are next shaken in a separating funnel with successive portions of a semi-saturated solution of potassium chloride in order to eliminate the iron, and are then evaporated in a partial vacuum at a low temperature, and the residue dried for an hour at 105°-110°, and dissolved in water. The solution is decomposed with iodine solution and sodium bicarbonate and left for twenty-four hours in a closed flask, after which the excess of iodine is titrated with standard sodium thiosulphate solution. Good results are obtained if the conditions are closely followed.

According to Schluttig and Neumann (*loc. cit.*) a "normal" ink must comply with the following tests :—

1. It must be a clear liquid, capable of filtration and free from suspended matter.
2. It must flow readily but not too rapidly from the pen, and must be retained by a properly sized paper.
3. It must keep well in an ink-pot, not becoming mouldy or forming a skin on the surface, and only gradually yield a slight deposit.
4. It must only give a slight varnish-like deposit on the pen.
5. It must not be too acid, so as to attack a pen too rapidly.
6. It must be free from unpleasant odour.
7. It must not pass through a paper of good quality.
8. It must give writing which is not sticky when dry.

(Speaking generally, coloured writing inks should also comply with the foregoing conditions.)

In the case of "normal" inks of Class II. the following requirement is also essential :—

9. It must give writing which is extremely dark after eight days, and cannot be rendered illegible by twenty-four hours' treatment with alcohol and water.

III   2 K

Inks of Class II. may have any desired composition, provided they answer the foregoing requirements.

"Normal" inks of Class I., however, must also comply with the following conditions :—

10. They must contain at least 6 g. of iron per litre.

11. They must contain sufficient gall substance to give writing which dries within eight days to an intense black, and then after treatment for several days with water and alcohol, still retains a certain degree of blackness.

Iron-gall inks of the present day contain :—

(1) The provisional colouring matter ; (2) gall substance extract and iron salt, which by interaction yield the true pigment, which, unlike the provisional colour, should not fade on exposure to light and air ; (3) added substances, such as gum or mineral acid, to give " body " to the ink or render it more stable. The provisional colours of " blue-black," " green-black," " violet-black " inks and the like are gradually masked by the oxidised iron tannate ; and, provided the ink is of the right composition, the writing eventually becomes black, while the temporary pigment fades away.

The chemical cause of this after-darkening of ink is described in several books on iron-gall inks, and for the present purpose it suffices to say that the darkening is a function of the phenolic group in the gallotannic or gallic acid. Phenolic substances free from nitrogen yield with iron salts pronounced colorations more or less permanent on paper, provided that they contain either two free hydroxyl groups in the *ortho*-position, or a free hydroxyl and a free carboxyl group also in the *ortho*-position towards each other.

Writing done with a good iron-gall ink ought to be completely "fast" towards the action of air and light, and when dry and fully developed should also resist the action of water. It has been found, however, that the colorations given with iron salts by those phenols which have only two free hydroxyl groups, or one hydroxyl and one carboxyl group in the *ortho*-position, are not sufficiently resistant to water. Sufficient permanency against the action of air, light, and water appears only to belong to the colorations given by those phenols which contain three free adjoining hydroxyl groups, and do not contain any disturbing groups, *e.g.* the nitro-group.

Hence the conclusion is justified that the characteristic tinctogenic group in gallic and gallotannic acids is the association of three phenolic hydroxyls in the *ortho*-position. A proof that the hydrogen atom of the hydroxyl group plays an active part in the reaction is afforded by the fact that the capacity of a phenol to produce stable colorations with iron salts is lost when the hydrogen atom is replaced by a radicle.

The hydrogen atoms of the benzene nucleus do not take any direct

part in the reaction, since they may be entirely or partially replaced without inhibition of the colour production. At the same time, such substitution has considerable influence upon the shade of the coloration. Thus the greater the acidity of the substituting radicle and the larger the proportion of hydrogen replaced, the paler becomes the colour.

The carboxyl group of gallic acid does not possess tinctogenic properties, since the esters give more pronounced colorations than the free gallic acid itself. All substances that possess the same tinctogenic atomic grouping as gallic and gallotannic acids (viz., three phenolic hydroxyls in the *ortho*-position) may be described as "gall substances," while the term "gall contents" may be applied to the proportion of such substances in an ink. In addition to gallic and gallotannic acids the following substances may be included among the gall substances:— Pyrogallol and all its derivatives, in which no substitution of the hydrogen atom of the three hydroxyl groups has taken place (*e.g.*, mono-, di-, and tribromopyrogallol), pyrogallol sulphonic acid, pyrogallol carboxylic acid, esters of gallic acid, mono- and dibromogallic acids and their esters, hæmatoxylin, etc. A comparison of the intensity of the colorations given by the different gall substances with iron salts shows that the colours produced by tannin are among the palest, while those given by gallic acid and its esters and by hæmatoxylin are much darker. An ink which contains merely 4 g. of iron and 30 g. of gallotannic acid does not give black but only grey writing.

Further experiments have also shown that the darker the colours of the iron gall compounds the greater their "fastness" towards light. This is a fact of great importance in judging the documentary value of an ink.

Hence tannin (gallotannic acid) cannot be regarded as the substance which, beyond all others, is the most suitable for the production of an ink of documentary value. Other compounds (and not only gallic acid) would give far better results.

For these reasons it would be advisable to substitute the requirements of Condition 11 (p. 514) for the official German standard of 30 g. of gallotannic and gallic acids derived exclusively from galls. Moreover, it is not possible to ascertain with certainty the origin of the gall substances in an ink.

Provided an ink contain a sufficient proportion of iron and gall substances, together with gum, mineral acid, etc., in suitably small amounts, such ink will possess documentary value.

A good method of ascertaining the value of an ink for this purpose is to make systematic comparative tests with the sample in question, and with a standard ink containing a known sufficient quantity of gall substances and of iron. These tests are described subsequently.

New Prussian Regulations.—In the Prussian regulations of 22nd May 1912,[1] inks are classified into (1) "documentary" and (2) "writing inks," the latter being subdivided into (A) "iron-gall inks" and (B) logwood and dyestuff inks.

(1) *Documentary Ink* is an iron-gall ink containing at least 27 g. of anhydrous gallotannic and gallic acids, and not less than 4 g. or more than 6 g. of iron per litre (ratio 4·5 : 1 and 6·75 : 1). It must keep at least fourteen days in the inkpot without deposit, etc., must flow readily, and yield writing which, after eight days' exposure, is not affected by water, 85 per cent. alcohol, or 50 per cent. alcohol.

(2) *Writing Inks* of class A must contain 18 g. of gallotannic and gallic acids, with at least 2·6 g. but not more than 4 g. of iron per litre (ratio 4·5 : 1 and 6·75 : 1). In other respects they must answer to the same tests as documentary inks. The inks of Class B are not officially examined.

The tannin is determined by the ethyl acetate method (*supra*, p. 513), the residue being regarded as gallotannic and gallic acids, when 0·1 g. thereof absorbs at least 0·5 g. of iodine, when left for twenty-four hours in contact with 25–50 c.c. of standard iodine solution (about 50 g. per litre) in the presence of 2 g. of sodium bicarbonate. If less iodine is absorbed the ink is not suitable for official purposes.

For the determination of iron the residue left on evaporating 10 c.c. of the ink is ignited, heated with 1–2 c.c. of hydrochloric acid (sp. gr. 1·124), the solution oxidised with 1–2 c.c. of chlorine water, evaporated to dryness, the residue dissolved in about 0·5 c.c. of warm hydrochloric acid, and the solution diluted with about 20 c.c. of water. About 1 g. of potassium iodide is then added, and the separated iodine immediately titrated with $N/10$ thiosulphate solution, the liquid being meanwhile heated to 55° to promote the further separation of iodine.

The tests of the permanency of the writing are applied in comparison with Schluttig and Neumann's standard ink as described on p. 520.

THE COMPOSITION OF ENGLISH INKS (C. A. Mitchell).

The standards enforced for writing ink in Germany have been adopted by several other countries. Thus, in the state of Massachusetts, U.S.A., all ink used for official purposes must answer to these requirements.[2]

In Great Britain no official standard for ink is published, but tests are made to see that the ink contains a sufficient quantity of gall

[1] Hinrichsen, *Chem. Zeit.*, 1913, **37**, 265.
[2] Information kindly communicated by Dr Bennett Davenport, Boston, U.S.A.

substances and iron, and that the writing done therewith is sufficiently permanent. The qualitative tests are similar to those used in Germany, and are described below.

The increasing use of fountain pens has led to the sale of a great deal of ink which flows freely from the pen, and drys to a good black, but which certainly does not contain sufficient tannin (gall substances) or iron to render the writing permanent against the action of light and air. An example of an ink of this kind is given in the subjoined Table.

The proportion of iron to gallotannic acid used by different English manufacturers shows wide variations, and it would seem that few attempts have been made to ascertain the correct proportions to assure the greatest degree of permanency for the writing.

From experiments made by O. Schluttig and G. S. Neumann, and by Mitchell,[1] it appears probable that the insoluble tannate produced when ink dries upon paper contains about 5·5 per cent. of iron, and would thus correspond in composition with the iron tannate described by Wittstein[2] and by Schiff.[3] It would therefore appear rational to base the relative proportions of the ingredients of an ink upon the amounts required to form this compound, and to avoid any material excess of either iron or gall substances.

An excess of the former certainly tends to cause the writing to turn brown, but further work is required to ascertain the effect of an excess of gallotannic or gallic acids upon the permanency of the writing. For further details on this question the reader may be referred to "*Inks: Their Composition and Examination,*" by C. A. Mitchell and T. C. Hepworth.

The wide variations in the amounts of the constituents of commercial inks is shown in the following Table, which gives the composition of several of the best known inks, typical of those on the English market.

Composition of Typical English Writing Inks.

	Water.	Total solids.	Ash.	Iron.	Sp. gr.
	Per cent.	Per cent.			
Blue-black ink	96·26	3·74	0·84	0·44	1·021
"	95·54	4·46	0·62	0·37	1·022
Japan ink	...	...	...	...	...
Logwood ink	97·86	2·14	1·04	0·40	1·015
"	95·16	4·84	1·10	trace	...
Fountain pen ink	97·52	2·48	0·42	0·18	1·014
Black (for documents)	92·16	7·84	1·45	0·54	...

[1] *Analyst*, 1908, 33, 82. [2] *Jahresber. d. Chem.*, 1848, 28, 221.
[3] *Ann. Chem. Pharm.*, 1875, 175, 176.

Other analyses will be found in the Table published by Mitchell,[1] who in 1908 found that out of twenty-four commercial samples the amount of solid matter ranged from 1·89-7·94 per cent., the ash from 0·42-2·52 per cent., and the iron in the iron-gall inks from 0·18-1·09 per cent.

QUALITATIVE EXAMINATION OF WRITING INKS.

The difficulties of forming an opinion upon the value of an ink are frequently increased by the presence of various dyestuffs and combinations of other substances, and in some cases it may be necessary to isolate special ingredients by extraction with ether, chloroform, etc.

In any case it is advisable to apply tests to the coloured washes given by the ink upon paper, and for this purpose the following "stripe" method enables uniform results to be obtained.

Schluttig's "Stripe" Method.

If the ink is made to flow from a small pipette across the surface of a piece of paper stretched in a frame which is kept inclined at an angle

FIG. 63.

of 45°, broad bands or stripes of colour are produced. The effects of tests applied to these may be followed much more readily than when reagents are applied to the writing itself.

The writing paper, which must be of uniform quality, is stretched by means of screws in an iron frame, which is then fixed at the proper angle.
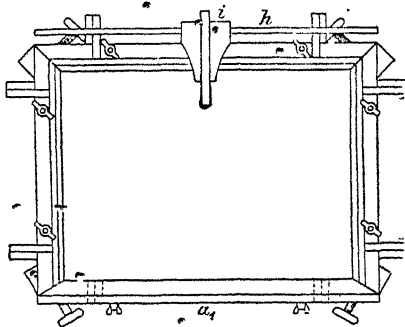
The construction of this frame is obvious from the diagram shown in Fig. 63.[2] It is provided with a channel at the bottom to catch the excess of ink, whilst the groove, i, is intended as a rest for the pipette, so that its point may always be applied to the surface of the paper at the same angle. The pipette delivers about 0·6 g. of ink, which produces a stripe about 6 mm. wide and 270 mm. in length. Care must be taken to prevent the formation of air bubbles.

Given parallel conditions, the breadth of the stripe and the amount of ink it contains will depend upon the degree of fluidity and adhesion of the ink to the paper. A point that may be borne in mind in the examination of copying inks is that the greater the copying

[1] Analyst, loc. cit., p. 81.

[2] The frame may be obtained from the Mechanische Institut of Oskar Leuner, Dresden.

power of an iron-gall ink the narrower the stripe. Inequalities and sources of error due to this cause may be eliminated by diluting the inks with equal quantities of distilled water.

In the absence of special apparatus comparable colour stripes may be made upon sheets of Bristol drawing board inclined at an angle of 45°.

Differential Reactions.

More or less separation of the constituents of an ink may be effected by letting a drop fall upon thick filter paper, when, owing to the different degrees of diffusion capacity, the resulting zones will contain a liquid of different composition. Or strips of ordinary filter paper may be immersed at one end in the ink, with the result that the liquid·as it rises will undergo some fractionation. Test reagents may then be applied to the different zones. It is preferable to dilute ordinary writing ink with an equal volume, and copying inks with three or four times their amount of distilled water before applying this method of fractionation.

In the case of iron-gall inks the outermost zone will be a light rust colour, due to a basic ferric salt, and on treatment with solutions of potassium bisulphate and potassium ferrocyanide will give the Prussian blue reaction.

Inks prepared from extracts of Chinese or small Asiatic galls, German oak-apples (*Knoppern*), dividivi, valonea, oak bark, chestnut bark, and logwood, as the "gall substance," will show, after the lapse of one or two days, an outer zone which is either of a light rust colour or which is tinted with the provisional colouring matter in the ink.

The innermost zone will be blue black, and in the case of inks prepared from galls or dividivi, will show a margin of characteristic lines, which will be entirely lacking in the case of the inks from tan barks or logwood.

Only in the case of sumach, and especially of myrobalans, does the black tint of the iron-gall compound extend into the outermost zone, so as to cause the latter to appear dark grey. Ink from myrobalans shows, between the outer and inner zone, a blue-black line on which is a light grey band, becoming black towards the middle. Both the sharp black line and the light grey band are absent in the case of sumach, and the uniform blue-black·inner zone abuts directly upon the yellowish-green outer zone.

With chrome logwood writing and logwood copying inks the outer zone is either entirely absent, or, in the case of the latter, is light grey and is free from iron. On the other hand, all logwood inks give a characteristic red coloration with sulphuric acid or sodium bisulphate solution.

Similar spotting tests may be applied to the stripes obtained in the "stripe" method. The presence of an iron-gall ink is indicated by the gradual darkening of such stripe, while by the use of various reagents information may be obtained with regard to other colouring matters in the ink.

The reactions given by inks of different colour and black inks containing provisional colouring matters are shown in the Tables on pp. 529-531.

PRACTICAL TESTS OF WRITING INKS.

1. Determination of the Darkening Capacity.

The darkening capacity of the sample of the ink in question is compared under parallel conditions with that of a standard iron-gall ink prepared in the laboratory from the following ingredients :—Tannin (puriss.), 23·4 ; gallic acid, 7·7 ; ferrous sulphate, 30·0 ; gum arabic, 10·0 ; hydrochloric acid, 2·5 ; and phenol, 1·0 g., in 1000 c.c. of water.

This ink is prepared by dissolving the tannin and gallic acid in water heated to about 50°, adding the other ingredients, and diluting the whole to 1 litre. After standing for at least four days in a moderately warm place (10°-15°), the clear supernatant liquid is decanted from any slight deposit. Filtration is to be avoided, if possible, owing to the fact that ordinary filter paper will absorb an appreciable amount of tannin.

The standard ink thus obtained will have a faint bluish-grey tint, and must be subsequently coloured so as to match any ink in question. This is not a difficult matter in the case of "blue-black," "green-black," etc., writing fluids, but the greatest care is required in preparing the standard to match an ink that flows immediately black from the pen. Such inks are usually coloured by the addition of relatively large amounts of various pigments (usually coal-tar dyestuffs); the proportion added, however, being limited by the injurious effect of an excessive quantity upon the fluidity of the ink. But, since, for the purposes of this test the ink is first diluted with an equal volume of water (*vide infra*), it is rendered paler for the comparison. Moreover, the "stripes" may be treated when dry with water and alcohol so as to extract all soluble pigments, and leave behind only the insoluble iron-gall compounds, the intensity of the colour of which may then be readily observed and matched.

In the preparation of suitably coloured inks the following dyestuffs may be used :—Bavarian blue, D.S.F ; Nacarate Red S. (Aktienges. Anilinfab., Berlin); Acid Green VBSPo, and Chestnut Brown (Oehler).

Thus, for example, inks of medium colour may be obtained by

adding the following amounts of these dyestuffs to 1 litre of the standard iron-gall ink :—

	Blue-black.	Green-black.	Red-black.	Immediate black.
	g.	g.	g.	g.
Blue dyestuff . .	2·2	1·0	...	2·5
Green ,, . .	...	2·5	...	0·5
Red ,, . .	...	...	2·5	...
Brown ,, . .	...	...	...	3·5

By increasing or reducing the quantities of these dyestuffs, or by mixing the coloured inks together in suitable proportions, any shade required may be matched.

In using the standard ink it should be borne in mind that it is not intended to represent the best obtainable sample of ink, but only one giving the lowest permissible limit for intensity and permanency of writing.

The tannin for the standard iron-gall ink should be such as is completely absorbed by hide powder in the usual method of estimation. The amount of iron is increased from the 4 g. of the official German standard to 6 g. (= 30 g. of ferrous sulphate), and part of the gallotannic acid is replaced by gallic acid in accordance with the equation :—

$$C_{14}H_{10}O_9 + H_2O = 2C_7H_6O_5.$$
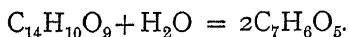
Owing to its sparing solubility, gallic acid cannot be added in greater proportion than 7·7 g. per litre, with the object of causing a more pronounced darkening of the writing.

In applying the darkening test about 15 c.c. of the ink under examination are withdrawn by means of a pipette from the bottle, care being taken not to disturb the contents. The bottle is then corked again in such a way that it can be opened without shaking, and is allowed to stand for three days in a moderately warm place (15°). In the meantime an ink is prepared from the standard iron-gall ink to match the sample previously withdrawn.

The two inks are then used in the preparation of stripes by the "stripe" method, both undiluted, and after the addition of an equal volume of water. The paper is left stretched in the frame until completely dry, after which it is removed from the frame and left for eight days exposed to the air and diffused daylight in a moderately warm place, care being taken to protect it from dust or acid fumes.

The stripes produced by the undiluted ink afford information as to the fluidity, penetrating capacity, and stickiness, while those given by the diluted ink are used in the tests of darkening capacity.

Should the stripes from the sample diluted not appear as dark as

those from the equally diluted standard ink, after the lapse of eight days, the former may be rejected as unsatisfactory without the necessity of applying further tests.

On the other hand, if the stripes from both inks appear of equal intensity, the paper should be cut into strips about 3 cm. broad, at right angles to the direction of the stripes. One of these strips is immersed in distilled water, a second in 85 per cent. alcohol, and a third in 50 per cent. alcohol. After two days they are withdrawn, dried at the ordinary temperature, and the relative intensities of colour of the residual stripes compared. The ink in question cannot be regarded as satisfactory, unless the stripes on all three strips are as dark as those of the standard ink.

The object of treating the strips with water and alcohol is to extract all substances which remain soluble after drying, so that the residual colour upon the paper affords a measure of the proportion of true gall-substances in the ink. For, as has already been pointed out, it is necessary to determine whether the darkening is due solely to substances which contain three neighbouring hydroxyl groups (i.e. true "gall-substances"), or whether it is partially or wholly due to those ortho-dihydroxy derivatives and ortho-hydroxycarboxylic acids which also yield colorations with iron salts that may be fixed upon paper. Experiments have shown that pyrocatechin (catechol) and protocatechuic acid will produce colorations which will resist the action of light but not of water, whereas the colorations given by ortho-hydroxycarboxylic acids are neither fast to light nor to water. Hence the water test affords a means of distinguishing between the two classes of compounds.

Acidity (C. A. Mitchell).—At the same time the degree of resistance offered by the colorations to water gives information as to the acidity of an ink. The greater the proportion and the strength of the free acid the more slowly does the writing darken. Any ink which, while containing a sufficient proportion of gall-substances, is so acid that the writing darkens insufficiently or too slowly, must be rejected.

Apart from its influence upon the writing, the acidity of an ink is also of importance from the point of view of its action upon steel pens. Several of the inks upon the English market give writing that darkens quite satisfactorily, but at the same time have a very drastic action upon pens. This high proportion of acid is not essential to the keeping or penetrating properties of the ink, seeing that in the inks of other manufacturers of equal repute a much lower acidity suffices.

The determination of the acidity of ink is not always an easy matter owing to the fact that, even after very great dilution, the dark colour of some inks prevents the change of colour of any indicator being seen sharply.

A method that has given good results in the case of very dark samples, is to heat 5 c.c. of the ink beneath a reflux condenser with 10-20 c.c. of hydrogen peroxide solution until the liquid becomes nearly colourless.   At the same time 5 c.c. of a solution of 1 g. of ferrous sulphate and 8 g. of gallotannic acid per 100 c.c. are heated with the same amount of hydrogen peroxide solution.   Both liquids are then titrated with standard alkali solution with methyl orange as indicator, and from the difference between the two results the amount of free acid in the ink may b. calculated.

Another practical test is to wash a steel pen with alcohol and ether and determine its weight when dry.   It is then immersed in 20 c.c. of the ink in a closed flask, and left for a given period (say a week), after which the pen is washed with water, alcohol, and ether, dried, and again weighed.

Very pronounced differences may be observed in the behaviour of different commercial inks in this test.   In the case of one well-known ink the loss in weight amounted to 5 per cent. of the original weight of the pen ; in another, the loss was less than half that amount.

Sulphuric acid has a more corrosive action upon pens than hydrochloric acid, and preference should be given to an ink containing the latter.

Proportion of Iron.—The amount of iron in an ink is determined as described above (p. 516), or gravimetrically.   If insufficient in quantity the ink may be rejected without further examination as unsuitable for documentary purposes.   It has already been pointed out, however, that there must be sufficient tannin to combine with all the iron.

2. The Stability of the Ink.

A well-made matured ink should keep for at least a year in a closed bottle without forming any deposit upon the sides, provided that it is not cooled too much.   An ink of good composition, however, will form such deposits if sent into the trade without having been stored long enough, or if it is left in a cold place.   Hence, the stability tests should always be applied to a clear filtered portion of the sample.   A well-matured ink ought to keep for at least six weeks when left in a dust-free place in a flask with a neck 1-2 cm. in diameter, provided that its volume is not less than 25 c.c., that it occupies at least half the capacity of the flask, and that the height of the body of liquid is greater than half its mean diameter.

The decomposition of iron-gall inks is the result of an oxidising process, which proceeds more rapidly in open than in closed flasks, and in the latter case only reaches a certain point.   The greater the surface of a given ink exposed to the air, the more rapidly does the

oxidation take place. Hence, it goes without saying, than in comparing the stability of different inks the conditions must be strictly analogous.

The following method of applying this test may be recommended :— About 50 c.c. of the ink, which has previously been left for three days in a closed bottle kept in a cool place (10°-15°), are withdrawn by means of a pipette, which is introduced into the middle of the fluid immediately after uncorking the bottle. This sample is rapidly filtered through the finest filter paper, precautions being taken to prevent excessive contact with atmospheric oxygen. 25 c.c. of the filtrate are then transferred to a cylindrical 500 c.c. flask with a flat bottom, and having a height of 185 mm. and a maximum diameter of 72 mm. The mouth of the flask is covered with a cap of filter paper to prevent the access of dust, and the flask itself, containing ink to the height of about 12 mm., is placed in diffused daylight in a room at the ordinary temperature, where it will not encounter acid or ammoniacal fumes.

If, before the lapse of fourteen days, films appear on the surface of the liquid, or deposits are formed on the walls or bottom of the flask, the ink must be rejected as unsatisfactory.

An ink which shows a deposit at the bottom of the sample bottle is not necessarily to be condemned, since, as was pointed out above, this may merely indicate insufficient storing. Further deposition, however, in the test sample taken as described indicates not want of maturity but progressive decomposition.

The formation of a film upon the surface of the ink is especially indicative of such decomposition, and any sample forming such a pellicle should be rejected without further examination.

The deposits upon the walls of the flask never occur without a simultaneous deposit at the bottom, or the formation of a film upon the surface. They may be regarded as intermediate in character between the two other kinds of deposit.

3. The Fluidity and Penetrating Capacity of the Ink and Stickiness of the Writing.

The simplest way of judging of the fluidity of an ink is to try it with a pen. But a rough test of its efflux velocity in running from a 50 c.c. pipette with a narrow outlet will afford means for a numerical comparison with a standard ink under the same conditions.

The form of the stripes in the stripe test will also afford information as to the fluidity. At the point where the pipette was applied to the paper, the ink will have spread so as to form an oval stain. In the case of most commercial writing inks this oval will show approximately the

same form, and the stripes will have the same breadth ; and as a rule, it is only the combined writing and copying inks that give stripes somewhat narrower than those from ordinary writing inks.

When, however, the ink is too fluid, and flows too rapidly from the pen, it will spread out over the paper with the result that the oval will be larger in area, and the breadth of the stripe will contract from the top downwards. The form and breadth of the stripes should therefore be compared with those of the stripes from the standard ink.

Comparative tests are also made as to the degree of penetration of both the standard ink and the sample with writing paper of good quality. The writing should not appear on the other side of the paper.

In the same way the standard ink is used as the basis of comparison in determining how long the writing remains sticky. Even in the case of copying inks an actual stickiness should not be perceptible when the writing is completely dry.

4. Identification of Different Inks.

In testing the identity of two given samples of ink, comparative determinations may be made of their respective ingredients. As is seen in the Table on p. 517 the inks made by different manufacturers vary widely in composition.

Further proofs may be obtained by determining the specific gravity, the stability and the viscosity of the respective inks, and by comparing the behaviour of the " stripes " in the stripe test when tested with water, alcohol, and different chemical reagents.

Their copying power may also be ascertained by pressing the paper with the stripes for three minutes beneath moist copying paper folded six times. The test should be made an hour after the stripes have been made, and again after the lapse of one or two days.

5. Differentiation of Inks in Writing (C. A. Mitchell).

The methods of distinguishing between different inks in writing is based upon the fact that manufacturers use varying proportions of iron salt and galls, and add either a different provisional colouring matter or different quantities thereof.

If a particular ink is to be compared with a given piece of writing a colour scale should be prepared from that ink, consisting of four washes ranging from the faintest to the darkest possible tone, and, if practicable, the paper should be left for about a week for the ink to undergo oxidation.

The scale may then be compared under the microscope with the

writing in question, and portions of equal intensity be submitted to comparative tests.

The following reagents will be found useful for the purpose :—

(1) Hydrochloric acid, 5 per cent.

(2) Oxalic acid, 5 per cent.

(3) Stannous chloride, 10 per cent.

(4) Nascent hydrogen, 50 per cent. hydrochloric acid with zinc.

(5) Bromine, saturated aqueous solution.

(6) Bleaching powder, saturated solution.

(7) Titanous chloride, commercial solution.

(8) Potassium ferrocyanide, 5 per cent. solution acidified with hydrochloric acid.

The colorations obtained should be compared under the microscope after five minutes, and again, next day, when dry.

As examples of the differences to be observed in writing done with various commercial inks, the following results may be quoted from Mitchell's Table.[1]

Reactions of English Inks in Handwriting while Moist.

Ink.	Hydrochloric acid.	Oxalic acid.	Stannous chloride.	Nascent hydrogen.
I.	Green-blue	Green-blue	Blue-violet	Violet
II.	Grey	Light grey	Grey	Pale pink
III.	Deep violet	Red-violet	Violet	Violet
IV.	Bright blue	Bright blue	Bright blue	Bright blue
V.	Deep blue	Deep blue	Violet	Violet-blue
VI.	Red	Pink violet	Blue-black	Pink violet

Ink.	Bromine.	Bleaching powder.	Titanous chloride.	Acidified potassium ferrocyanide.
I.	Deep violet	Greenish	Dirty green	Green-blue
II.	Little action	Slight bleaching	Light orange	Green-black
III.	Violet-black	Yellow on violet	Deep maroon	Deep violet
IV.	Dark purple	Slight bleaching	Green-grey	Dark blue
V.	Slight bleaching	Surface bleaching	Nearly black	Deep green-blue
VI.	Surface bleaching	,,	Maroon	Violet-black

It is possible, care being taken, to test characters of equal intensity, to distinguish between writing that has been done several years, and that which has been done comparatively recently with the same ink.

The more recently applied ink will react much more rapidly and intensely, especially with acid reagents; and in some instances a reagent will cause pronounced smudging, which only gradually ceases as the writing ages.

[1] *Analyst*, 1908, 33, 84.

II. COPYING INKS.

It is not always possible to make a sharp distinction between writing and copying inks, since the former will generally yield one or more copies for a short time after writing.

Commercial preparations sold under the name of "Writing and Copying Inks" may be regarded as copying inks, provided they will give a clear copy two days after writing. In other respects they should comply with the requirements of a good writing ink.

In the case of inks not intended for copying purposes, the amounts of pigments, ready formed and latent, are usually insufficient to give copies without leaving the original writing too pale.

Hence the ingredients of copying inks must be concentrated in proportion to the number of copies required. The statement frequently found in the text-books that copying inks only differ from writing inks in containing a larger proportion of hygroscopic and glutinous substances, such as sugar, dextrin, glycerine, gums and the like, is only partially true.

In examining copying inks by the "stripe" test, the sample should be diluted with three or four times its volume of water, the amount of dilution depending upon the concentration of the ink. The results will then be comparable with those given by writing inks diluted with an equal quantity of water.

Tests should also be applied on the lines described under "Writing Inks" to the residual writing, after the copies have been taken.

The copies should be sharp, should dry rapidly, and not remain sticky. Otherwise the presence of too much hygroscopic matter in the ink is indicated.

In testing the copying power the paper with the stripes is placed beneath moistened copying paper (which is folded six or eight times), and pressed for three minutes in a copying press.

Similar tests are made after the stripes have dried for twenty-four and forty-eight hours, and the results will show the rate at which the copying power of an ink diminishes as the writing dries.

III. COLOURED WRITING INKS (C. A. Mitchell).

In the earlier kinds of coloured writing inks, various metallic pigments such as verdigris, or vegetable dyestuffs such as indigo, logwood and madder, were used. Or, in some cases, animal products such as the juice of the mollusc (*murex*) or cochineal were employed. The discovery of the aniline dyestuffs, however, led to a gradual change in the manufacture of coloured inks, and the older, and, in many cases

more permanent pigments, are now only used to a limited extent, and then usually in association with aniline dyestuffs.

The relative degree of permanency of the older pigments is shown by the results of the experiments of Russell and Abney.[1] The aniline dyestuffs are, speaking generally, very fugitive, and cases are on record where writing done with aniline inks has become illegible in six months.

In some respects, however, they are more resistant to the action of chemical agents than the black iron tannate formed in iron-gall inks. On this fact depend some of the tests for distinguishing between black inks containing different provisional pigments (cf. p. 529).

Among the aniline dyestuffs suitable for use as coloured writing inks are the following products (BASF) :—

Red : eosin, erythrosin, and phloxin ; ponceau scarlet ; cotton scarlet.

Green : neptune green, SG ; light green, SF (yellowish) ; light green, SF (bluish) ; diamond green, G and B.

Blue : indigo carmine ; soluble blue, T.

Violet : acid violet, 4 BL.

Yellow : fast yellow ; tartrazine.

Solutions containing from 1·5-3 per cent. of these dyestuffs yield inks which flow well, and are thus particularly suitable for stylographic pens.

Tests for Coloured Inks.

The following Tables show the reactions given by different groups of typical coloured inks, and by iron-gall inks containing dyestuffs to give the respective provisional colours. To apply the reactions the inks are diluted in each case with an equal volume of water, and a series of stripes prepared by the " stripe method." These are allowed to dry for at least a day, exposed to pure air, and are then tested with a drop of the respective reagents, the alterations in colour being recorded immediately, and also after the lapse of twenty-four hours.

I. Blue and Blue-black Inks.

(1) Soluble Prussian blue, from 0·3 per cent.

(2) Sodium indigo-sulphonate, 0·1 per cent.

(3) Bavarian blue, DSF, 1·2 per cent.

(4) Methylene blue, 0·5 per cent.

(5) Blue-black ink (p. 520).

[1] *Report to Science and Art Depart.,* 1888.

	Sodium hydroxide, 2·5 per cent.	Sulphuric acid, 5 per cent.	Oxalic acid, 1 5 per cent.	Sodium carbonate, 5 per cent.
1. Immediately	White	Unchanged	Unchanged	White
After 24 hours	White, with yellow edge	Darker blue	Darker blue	,,
2. Immediately	Yellow	Unchanged	Unchanged	Lighter blue
After 24 hours	White, with yellow edge	White	White	Light grey-blue
3. Immediately	Brown	Darker blue	Darker blue	Black-blue
After 24 hours	White, with yellow edge	,,	,,	Light yellow, with green edge
4. Immediately	Violet	Lighter blue	Lighter blue	Light blue
After 24 hours	Green-blue, with green edge	White, with green edge	,,	Green-blue
5. Immediately	Brown	Lighter blue	Lighter blue	Brown-blue
After 24 hours	,,	Grey-blue	,,	Brown

	Sodium bisulphate, 5 per cent.	Sodium sulphite, 5 per cent.	Potassium oxalate, 5 per cent.	Stannous chloride, 5 per cent. +Hydrochloric acid, 5 per cent.
1. Immediately	Unchanged	Violet blue	Light grey	Unchanged
After 24 hours	Darker blue	White to light grey	White	,,
2. Immediately	Unchanged	Lighter blue	Unchanged	White
After 24 hours	White	White	Light blue-grey	,,
3. Immediately	Darker blue	,,	Unchanged	Unchanged
After 24 hours	,,	,,	Light blue-green	Darker blue
4. Immediately	Lighter blue	Lighter blue	Lighter blue	White
After 24 hours	,,	Light blue	Light blue	,,
5. Immediately	Light blue	Red-grey	Unchanged	Light blue
After 24 hours	,,	Brown	Brown	Grey-blue with green edge

II. Green and Green-black Inks.

	Ammonia solution, 5 per cent.	Sodium hydroxide, 2·5 per cent.	Sodium carbonate, 5 per cent.	Sodium sulphite, 5 per cent.
6. Immediately	White	White	Lighter green	White
After 24 hours	Light green	White, with yellow edge	White	,,
7. Immediately	Light green	Light green	Lighter green	Light green
After 24 hours	,,	White, with yellow edge	Light green	Pale green
8. Immediately	Green-brown	Brown	Brown-green	Grey-green
After 24 hours	,,	,,	Brown	Brown

	Borax, 5 per cent.	Nitric acid, 5 per cent.	Sulphuric acid, 5 per cent.
6. Immediately	Light green	Light green	Light green
After 24 hours	White	White, with grey edge	White
7. Immediately	Unchanged	Light yellow-green	Light yellow-green
After 24 hours	Lighter green	White, with grey-green edge	White, with yellow edge
8. Immediately	Grey-brown	Light blue-green	Light blue-green
After 24 hours	Brown	Grey-blue	Green-blue

(6) Acid green, 1·2 per cent.

(7) Malachite green, 0·2 per cent.

(8) Typical green-black ink (p. 521).

III. Red and Red-black Inks.

(9) Nacarate, S, 0·5 per cent.

(10) Fuchsine, F, 0·2 per cent.

(11) Eosin, A, 1·5 per cent.

(12) Carmine, 1·65 per cent. + ammonia 0·7 per cent.

(13) Typical red-black ink.

	Sodium hydroxide, 8·5 per cent.	Sulphuric acid, 1·5 per cent.	Oxalic acid solution, 1·5 per cent.
9. Immediately	Yellow-grey	Unchanged	Unchanged
After 24 hours	White, with grey-red edge	Grey-red	Light grey-red
10. Immediately	Light red	Light grey	Unchanged
After 24 hours	Pale red	White	Light blue-grey
11. Immediately	Yellow red	Light yellow	Yellow
After 24 hours	White, with orange-red	"	"
12. Immediately	Red-grey	Unchanged	Unchanged
After 24 hours	White, with dark red edge	Brown-red	"
13. Immediately	Grey-red	Light red	Light red
After 24 hours	Brown	"	"

	Sodium carbonate solution, 5 per cent.	Sodium bisulphate, 5 per cent.	Stannous chloride and hydrochloric acid.
9. Immediately	Red-grey	Unchanged	Unchanged
After 24 hours	"	Light red	Bright grey, with violet edge
10. Immediately	Unchanged	Red-grey	White
After 24 hours	"	Light blue-grey	White, with dark green edge
11. Immediately	Yellow-red	Yellow	Light yellow
After 24 hours	"	"	
12. Immediately	Red-grey	Unchanged	Unchanged
After 24 hours	"	Light red	
13. Immediately	Brown	Light red	Light red
After 24 hours	"	"	White, with red edge

IV. Violet and Brown Inks.

(14) Methyl violet, 0·3 per cent.

(15) Chrome logwood ink, containing 2 per cent. logwood extract, 0·3 per cent. of potassium chromate, and 2 per cent. of sodium carbonate.

(16) Tungsten ink, containing 4·5 per cent. of logwood extract, 1·5 per cent. of sodium tungstate, 0·4 per cent. of tartaric acid, and 0·03 per cent. of salicylic acid.

(17) Logwood copying ink, containing 8 per cent. of logwood extract, 2 per cent. of aluminium sulphate, 0·5 per cent. of

oxalic acid, 4 per cent. of ammonium oxalate, 1 per cent. of glucose, 0·5 per cent. of potassium bichromate, and 0·15 per cent. of salicylic acid.   Dries violet-black.

(18) Alizarin, 2·5 per cent., and ammonia solution, 1·0 per cent. Dries brown.

	Ammonia solution, 5 per cent.	Sodium hydroxide, 2·5 per cent.	Sulphuric acid, 5 per cent.	Sodium sulphite, 5 per cent.
14. Immediately .	Unchanged	Violet	Light green	Light violet
After 24 hours .	Light violet	Light grey	Yellow-grey	,,
15. Immediately .	Unchanged	Light yellow	Grey-red	Unchanged
After 24 hours .	,,	Grey-yellow	Grey-red, with dark red edge	Light grey
16. Immediately .	Red-blue	Grey-violet	Red-violet	Light yellow
After 24 hours .	Violet-black	Grey-yellow, with brown edge	Dark red	,,
17. Immediately .	Blue	Brown, with blue edge	Yellow-red	Grey-violet
After 24 hours .	Violet-black	Grey-yellow, with brown edge	,,	Light grey
18. Immediately .	Dark red	Blue, with red edge	Light yellow	Violet
After 24 hours .	,,	Light brown, with dark edge	,,	Dark red

	Borax, 5 per cent.	Copper sulphate, 5 per cent.	Stannous chloride and hydrochloric acid.
14. Immediately .	Unchanged	Unchanged	Light grey-blue
After 24 hours .	Lighter violet	Violet	White, with green edge
15. Immediately .	Unchanged	Unchanged	Grey-violet
After 24 hours .	Light grey	,,	Light grey-red, with dark red edge
16. Immediately .	,,	,,	Red-violet
After 24 hours .	,,	Blue-black	Dark red
17. Immediately .	Blue	Dark grey-blue	Red-violet
After 24 hours .	Light violet	Blue-black	Dark red
18. Immediately .	Red-brown	Brown	Yellow
After 24 hours .	Dark red	,,	,,

V. Black Inks.

	Sodium hydroxide, 2·5 per cent.	Sodium carbonate, 25 per cent.	Sulphuric acid, 5 per cent.	Sodium sulphite, 5 per cent.	Stannous chloride.
19. Immediately .	Brown-red	Grey-violet	Dark blue	Yellowish red	Dark blue
After 24 hours .	Red-grey, with dark red edge.	Grey-red	Dark blue, with violet edge	Light brown	,,
20. Immediately .	Light grey	Violet-grey	Grey	Violet-grey	Blue-grey
After 24 hours .	,,	,,	Grey-blue	,,	,,
21. Immediately .	Brown	Brown	,,	Brown-violet	,,
After 24 hours .	,,	,,	,,	Brown	Grey-blue
22. Immediately .	Green-blue	Bluish-green	Light grey	Unchanged.	Grey-yellow
After 24 hours .	Yellow-grey	,,	Light yellow-grey	Brown	,,
23. Immediately .	Unchanged	Unchanged	Unchanged	Unchanged	Unchanged
After 24 hours .	,,	,,	,,	,,	,,

(19) Black ink containing 1·2 per cent. of Bavarian blue, 0·3 per
    cent. of acid green, 1·5 per cent. of chestnut brown. Flows
    blue-black and dries grey-black.
(20) Nigrosine ink, containing 1·25 per cent. of nigrosine.
(21) Typical iron-gall ink.
(22) Vanadium ink containing 10 per cent. of tannin, and 0·4 per
    cent. of ammonium vanadate. Dries grey-green.
(23) Carbon ink containing 10 per cent. of lampblack, 6·5 per cent.
    of shellac, and 6·5 per cent. of borax.

None of the foregoing inks resisted the action of sodium hypo-
chlorite, with the exception of No. 23, the pigment of which consisted
of lampblack. All the others were immediately bleached.

The reagents mentioned in the preceding Tables have only been
selected as illustrative examples. Obviously many others might be
used, and in special cases prove more characteristic.

IV. DRAWING INKS (C. A. Mitchell).

The inks specially prepared for the use of artists include solid and
liquid preparations of Indian Ink and of sepia, and the so-called black
and coloured "waterproof inks."

Indian Inks.

These consist of the finest lampblack thoroughly incorporated with
glue, and preserved by the addition of an antiseptic aromatic oil. The
quality depends chiefly upon the fineness of division of the lampblack
and the thoroughness of its incorporation with glue, and considerable
differences may be observed between different commercial samples in
this respect.

The following Table shows the composition of four kinds of Indian
ink arranged in descending order according to their quality and
price :—

Indian inks.	Water.	Carbon in insoluble residue.	Nitrogen in residue.	Nitrogen in original ink.	Ash.
	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.
I.	8·16	53·20	0·0	7·74	4·08
II.	7·20	52·53	...	4·87	3·69
III.	9·93	49·64	...	7·26	4·96
IV.	9·40	57·04	...	6·84	4·01

The practical tests to be applied to solid Indian ink include estimations of its solubility, covering power, and blackness of pigment.

For this purpose, 0·1 g. of the sample is powdered, and mixed with 10 c.c. of cold water, and a note taken of the time required to colour the liquid.

The rate of sedimentation of the carbon after complete incorporation of the ink and water should also be observed.

In testing the tinctorial value, either the liquid inks may be applied in successive washes with a pelt brush to Whatman paper pinned upon a slanting board, or Schluttig's stripe method may be used.

In the case of cheaper grades of ink, the washes will be found to be paler and to show coarse particles of carbon which produce streaks, while more washes are required to obtain opacity.

The liquid preparations upon the market are prepared from the broken, unsaleable fragments of the solid sticks. They may be examined by similar methods.

Sepia.

The pigment known as sepia is obtained from the "ink-sac" of the cuttlefish, *Sepia officinalis*, and other species of Cephalopoda. The dried ink-sacs are powdered and extracted with boiling sodium hydroxide solution and the pigment precipitated with hydrochloric acid, and washed and dried at a low temperature. It is sold in the powdered condition, or incorporated with a binding material into cakes.

It contains an amorphous acid, termed *sepiaic acid*, which contains 12·3 per cent. of nitrogen.

Some of the commercial samples of sepia contain a certain proportion of lampblack. The proportion of the latter may be estimated by treating the powdered sample with boiling water and examining the insoluble residue. In the case of pure sepia it will contain a large proportion of nitrogen, and will leave over 3 per cent. of ash on ignition. Lampblack preparations, on the other hand, give an insoluble residue consisting of nearly pure carbon, and containing only traces of nitrogen and mineral matter.

In comparing different samples of sepia attention should be given to its covering power and to the intensity of the pigment, as described under "Indian Inks."

Sepia, though commonly looked upon as a permanent pigment, has been shown by experiments of Russell and Abney[1] to fade materially after long exposure to light and air.

[1] *Loc. cit.*

Waterproof Inks.

These consist of lampblack or pigments of various colours dissolved or suspended in a liquid medium, such as an alcoholic solution of a resin, which on evaporation leaves an insoluble deposit which is not affected by water.

In examining these the various tests described above may be applied, and in addition to these the behaviour of the dried ink on paper towards water must also be observed.

V. Printing Inks (C. A. Mitchell).

Printing inks consist essentially of an insoluble pigment, such as lampblack, Prussian blue, etc., incorporated with boiled linseed oil, or other rapidly drying vegetable oil.

Their composition is of subsidiary importance to their behaviour in practice, and in examining them practical tests should be made of their covering power, drying capacity, and the intensity of the dried pigment.

In the case of some of the more delicate tints aniline dyestuffs incorporated with inert substances, such as china clay, transparent alumina, etc., are employed, and these are characterised by their lack of permanency on exposure to light and air.

The so-called " double-tone " inks consist of selected mixtures of pigments of secondary and tertiary colours, and a half-tone block printed with one of these products will give the effect of two printings, provided there is sufficient contrast between the light and dark portions.

VI. Ticket and Stencilling Inks (C. A. Mitchell).

The special properties required in this class of inks are rapid drying capacity and sufficient consistency not to smudge readily.

Many of the stencilling inks contain nigrosine in a suitably thickened medium, and are quite permanent enough for marking packing cases, and the like. In fact they resist the action of acid or acid fumes better than any iron-gall ink, though they smudge on contact with alkali.

Other inks consist of a basis of shellac and borax, with a suitable addition of lampblack or ultramarine.

The ticket inks are frequently solutions of aniline dyestuffs with additions to give " body " and to increase the rate of drying.

In other cases a mixture of lampblack, asphaltum, Venice turpentine, and turpentine oil is used for this purpose.

A rapidly drying ink used for rubber stamps was found to consist

of 1·38 per cent. of aniline dyestuff (a mixture of methyl violet and methylene blue) dissolved in dilute alcohol (60 per cent.), and containing 15 per cent. of glycerol and 8 per cent. of phenol.

The general methods of examining these inks have been described above.

VII. MARKING INKS (C. A. Mitchell).

The juices of various plants have long been used in different parts of the world to produce permanent marks upon textile materials. For example, different species of *Rhus* yield a juice which turns black on exposure to the air, while from the fruits of *Anacardium orientale*, "the Indian marking nut," an ink is prepared which produces an intense and lasting stain. Natural inks of this kind are employed as varnishes, and also enter into the composition of certain commercial marking inks.

Of the chemical preparations, those having as their basis a solution of a silver salt in a readily reducible form are the most widely used. Many of them consist of a solution of silver tartrate in dilute ammonium hydroxide, with the addition of a gum to thicken the liquid, and a small amount of some vegetable colouring matter. On applying heat to the writing done with such ink, the silver is reduced upon the fibres in the form of a very stable insoluble black oxide.

Numerous additions to silver marking inks have been patented during the last fifty years, but not many of these appear to have been commercially successful, although a small proportion of platinum is still found in certain preparations.

The following analysis shows the percentage composition of a typical sample of good marking ink :—

Water.	Free ammonia.	Mineral matter.	Silver.	Combined tartaric acid.	Gums.	Platinum.
76·93	4·87	12·30	9·98	6·83	3·94	0·26

Next to silver preparations in commercial importance come the aniline marking inks, which are usually sold in the form of two liquids to be kept separate until just before use. By the interaction of these, aniline black is deposited in an insoluble form upon the fibres of the fabrics, and produces very permanent marks. One of the portions of such an ink may consist of a solution of aniline hydrochloride, while the other may contain copper chloride, sodium chlorate, and ammonium chloride in suitable proportions.

Similar preparations for the production of indigo blue by the interaction of two ingredients have also been put upon the market.

For further particulars of the composition of these and other marking inks reference may be made to Mitchell and Hepworth's "*Inks.*"

The Examination of Marking Inks.

The composition of a marking ink is of less importance than its behaviour in practice, and in examining a sample systematic tests should be made to ascertain to what extent it answers to the following requirements :—

1. It is essential that it shall not injure the fibres of a fabric. In the case of certain aniline inks the effect of dry heat prior to washing is to render the marked places very brittle.

The addition of certain metallic oxides to an ink is also likely to affect the fibres in such a way that if they subsequently come into contact with a bleaching solution they will readily be disintegrated.[1]

2. When applied to the fabric, and gently heated or otherwise developed, the ink must yield marks of full blackness.

3. The marks must not fade on exposure to light or air, or when washed with soap and water and sodium carbonate. They should also offer a fair amount of resistance to the action of an acidified solution of bleaching-powder, which they may be liable to encounter in many laundries.

4. The ink should flow with sufficient ease from a pen and yet not be fluid enough to "run" upon the fabric.

5. It should keep well in a closed vessel in the dark and not yield an excessive amount of deposit.

VIII. Typing Inks (C. A. Mitchell).

These consist of a soluble pigment such as methyl violet, dissolved in a mixture of water and glycerol.

There are also black typing inks upon the market which, containing carbon, offer great resistance to the action of acids, alkalis, and bleaching solution.

The practical tests should include trials of the suitability of the ink for its special purpose, and of the permanency of the typed document.

The aniline typing inks are readily smudged by water and are not permanent when exposed to the action of light and air.

IX. Inks for Writing on Metals, Glass, Etc. (C. A. Mitchell).

Inks for metals usually contain a particular ingredient that will act upon the metal in question. Thus, an ink for writing on zinc labels

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[1] Cf. Higgins, *J. Soc. Chem. Ind.,* 1911, 30, 1296.

contains potassium chlorate and copper sulphate dissolved in water and thickened with gum.

A black ink for writing on metal surfaces in general consists of copal resin, turpentine oil, and lampblack, or vermilion.

Inks for writing upon glass are frequently nothing more than dilute solutions of hydrofluoric acid.

Others consist of a basis of turpentine oil, shellac, and Venice turpentine, with lampblack or other insoluble pigment.

The methods of examining these and similar preparations must obviously include tests as to their suitability for the purpose in question, and of the permanency of the writing.

X. SYMPATHETIC INKS (C. A. Mitchell).

Although sympathetic inks are in many cases merely curiosities, they yet may have some commercial importance owing to the fact that their use has been claimed in numerous patents. For example, a process has been devised for detecting any tampering with an envelope by means of steam, the two colourless ingredients of the ink being kept apart by a layer of dextrin.

The following Table includes some of the more common substances used as sympathetic inks, and shows the treatment required to render the writing visible.

Colour.	Ink.	Treatment with
Black or brown	Lead acetate Mercuric chloride Tannin Silver salt	A soluble sulphide Stannous chloride A soluble iron salt Action of light
Blue	Starch Cobalt nitrate Iron sulphate	Iodine Oxalic acid Potassium ferrocyanide
Yellow	Copper chloride Basic lead acetate Antimony chloride	Action of heat Hydriodic acid Tannin
Green	Cobalt chloride, with a nickel salt Potassium arsenate	Action of heat Copper nitrate
Purple	Gold chloride	Stannous chloride
Golden	Sodium gold chloride	Oxalic acid (10 per cent.) followed by heat

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END OF PART I.